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Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Supplement

Battelle Columbus Labs., OH

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Determination of toxic organic compounds in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analysis procedures. This methods compendium has been prepared to provide a standardized format for such analytical procedures. A core set of five methods covering 29 air toxic compounds was presented in the original document. In an effort to update the original compendium, four new specific methods have been added. With this addition, the compendium now contains nine standardized sampling and analysis procedures covering 36 air toxic compounds. As advancements are made, the current methods may be modified from time to time along with new additions to the compendium.

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COMPENDIUM OF METHODS FOR THE DETERMINATION OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR

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N O T I C E

SUPPLEMENT TO COMPENDIUM OF METHODS FOR THE DETERMINATION OF TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR

To holders of Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (EPA-600/4-84-041), dated April 1984:

The accompanying document is a supplement to the Compendium referenced above and contains the pages necessary to update the Compendium as of September 1986. The supplement is only an update and is intended to be used in conjunction with the original Compendium published by the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, in April 1984 (EPA-600/4-84-041). Copies of this document may be obtained, as supplies permit, from:

U. S. Environmental Protection Agency
Center for Environmental Research Information
Compendium Registration
26 W. St. Clair Street
Cincinnati, Ohio 45268
Attention: Distribution Record System

Copies of the Compendium dated September 1986 will contain the supplement.

Included in this supplement are all revisions pertinent to the update, along with instructions for merging the supplementary pages with the original document. Four new methods are added to the Compendium, and a new title page, Table of Contents, and new Tables 1 and 2 are included to reflect the added methods.

Any questions, comments, or suggestions regarding this supplement or the Compendium should be directed to the U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, MD-77, Research Triangle Park, NC, 27711; (919) 541-2665, (FTS: 629-2665).

Instructions for Merging the Supplement with the Compendium:

Delete	Insert
Original Title Page (4/84)	New Title Page (9/86)
Original Disclaimer, page ii (4/84)	New Disclaimer, page ii (9/86)
Original CONTENTS, page iii (4/84)	New CONTENTS, page iii (9/86)
Pages iv through viii (4/84)	Pages iv through viii (9/86)
-	Method TO6 (9/86)
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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Determination of toxic organic compounds in ambient air is a complex task, primarily because of the wide variety of compounds of interest and the lack of standardized sampling and analysis procedures. This methods compendium has been prepared to provide a standardized format for such analytical procedures. A core set of five methods is presented in the original document. In an effort to update the original Compendium, an addition of four specific methods has been made. With this addition, the Compendium now contains nine standardized sampling and analysis procedures. As advancements are made, the current methods may be modified from time to time along with new additions to the Compendium.

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INTRODUCTION

This Compendium has been prepared to provide regional, state, and local environmental regulatory agencies, as well as other interested parties, with specific guidance on the determination of selected toxic organic compounds in ambient air. Recently, a Technical Assistance Document (TAD) was published which provided guidance to such persons (1). Based on the comments received concerning the TAD the decision was made to begin preparation of a Compendium which would provide specific sampling and analysis procedures, in a standardized format, for selected toxic organic compounds.

The current Compendium consists of nine procedures which are considered to be of primary importance in current toxic organic monitoring efforts. Additional methods will be placed in the Compendium from time to time, as such methods become available. The original methods were selected to cover as many compounds as possible (i.e., multiple analyte methods were selected). The additional methods are targeted toward specific compounds, or small groups of compounds which, for various technical reasons, cannot be determined by the more general methods.

Each of the methods writeups is self contained (including pertinent literature citations) and can be used independent of the remaining portions of the Compendium. To the extent possible the American Society for Testing and Materials (ASTM) standardized format has been used, since most potential users are familiar with that format. Each method has been identified with a revision number and date, since modifications to the methods may be required in the future.

Nearly all the methods writeups have some flexibility in the procedure. Consequently, it is the user's responsibility to prepare certain standard operating procedures (SOPs) to be employed in that particular laboratory. Each method indicates those operations for which SOPs are required.

Table 1 summarizes the methods currently in the Compendium. As shown in Table 1 the first three methods are directed toward volatile nonpolar compounds. The user should review the procedures as well as the background material provided in the TAD (1) before deciding which of these methods best meets the requirements of the specific task.

Table 2 presents a partial listing of toxic organic compounds which can be determined using the current set of methods in the Compendium. Additional compounds may be determined by these methods, but the user must carefully evaluate the applicability of the method before use.

Reference

1. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air", EPA-600/4-83-027, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

TABLE 1. LIST OF METHODS IN THE COMPENDIUM

Method Number	Description	Types of Compounds Determined
TO-1	Tenax GC Adsorption and GC/MS Analysis	Volatile, nonpolar organic (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C.
TO-2	Carbon Molecular Sieve Adsorption and GC/MS Analysis	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15° to +120°C.
TO-3	Cryogenic Trapping and GC/FID or ECD Analysis	Volatile, nonpolar organics having boiling points in the range of -10° to +200°C.
TO-4	High volume PUF Sampling and GC/ECD Analysis	Organochlorine pesticides and PCBs
TO-5	Dinitrophenylhydrazine Liquid Impinger Sampling and HPLC/UV Analysis	Aldehydes and Ketones
TO-6	High Performance Liquid Chromatography (HPLC)	Phosgene
TO-7	Thermosorb/N Adsorption	N-Nitrosodimethylamine
TO-8	Sodium Hydroxide Liquid Impinger with High Performance Liquid Chromatography	Cresol/Phenol
TO-9	High Volume Polyurethane Foam Sampling with High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)	Dioxin

TABLE 2. LIST OF COMPOUNDS OF PRIMARY INTEREST

Compound	Applicable Method(s)	Comments
Acetaldehyde	TO-5	
Acrolein	TO-5	
Acrylonitrile	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Allyl Chloride	TO-2, TO-3	TO-3 yields better recovery data than TO-2.
Benzaldehyde	TO-5	
Benzene	TO-1, TO-2, TO-3	TO-3 yields better recovery data.
Benzyl Chloride	TO-1, TO-3	
Carbon Tetrachloride	(TO-1?), TO-2, TO-3	Breakthrough volume is very low using TO-1.
Chlorobenzene	TO-1, TO-3	
Chloroform	(TO-1?), TO-2, TO-3	Breakthrough volume is very low using TO-1
Chloroprene (2-Chloro-1,3-butadiene)	TO-1, TO-3	The applicability of these methods for chloroprene has not been documented.
Cresol	TO-8	
4,4'-DDE	TO-4	
4,4'-DDT	TO-4	
1,4-Dichlorobenzene	TO-1, TO-3	
Dioxin	TO-9	
Ethylene dichloride (1,2-Dichloroethane)	(TO-1?), TO-2, TO-3	Breakthrough volume very low using TO-1.
Formaldehyde	TO-5	
Methyl Chloroform (1,1,1-Trichloroethane)	(TO-1?), TO-2, TO-3	Breakthrough volume very low using TO-1.
Methylene chloride	TO-2, TO-3	
Nitrobenzene	TO-1, TO-3	
N-Nitrosodimethylamine	TO-7	

TABLE 2. (Continued)

Compound	Applicable Method(s)	Comments
Perchloroethylene (Tetrachloroethylene)	TO-1, (TO-2?), TO-3	TO-2 performance has not been documented for this compound.
Phenol	TO-8	
Phosgene	TO-6	
Polychlorinated biphenyls (PCBs)	TO-4	
Propanal	TO-5	
Toluene	TO-1, TO-2, TO-3	
Trichloroethylene	TO-1, TO-2, TO-3	
Vinyl Chloride	TO-2, TO-3	
Vinylidine Chloride (1,1-dichloroethene)	TO-2, TO-3	
o,m,p-Xylene	TO-1, TO-3	

METHOD FOR THE DETERMINATION OF PHOSGENE IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of phosgene in ambient air, in which phosgene is collected by passage of the air through a solution of aniline, forming carbanilide. The carbanilide is determined by HPLC. The method can be used to detect phosgene at the 0.1 ppbv level.

1.2 Precision for phosgene spiked into a clean air stream is ±15-20% relative standard deviation. Recovery is quantitative within that precision, down to less than 3 ppbv. This method has been developed and tested by a single laboratory(1), and, consequently, each laboratory desiring to use the method should acquire sufficient precision and recovery data to verify performance under those particular conditions. This method is more sensitive, and probably more selective, than the standard colorimetric procedure currently in widespread use for workplace monitoring(2).

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis(3).

2.2 Other Documents

Standard NIOSH Procedure for Phosgene(2).
U.S. EPA Technical Assistance Document(4).

3. Summary of Method

3.1 Ambient air is drawn through a midget impinger containing 10 mL of 2/98 aniline/toluene (by volume). Phosgene readily reacts with aniline to form carbanilide (1,3-diphenylurea), which is stable indefinitely.

3.2 After sampling, the impinger contents are transferred to a screw-capped vial having a Teflon-lined cap and returned to the laboratory for analysis.

3.3 The solution is taken to dryness by heating to 60°C on an aluminum heating block under a gentle stream of pure nitrogen gas. The residue is dissolved in 1 mL of acetonitrile.

3.4 Carbanilide is determined in the acetonitrile solution using reverse-phase HPLC with an ultraviolet absorbance (UV) detector operating at 254 nm.

4. Significance

4.1 Phosgene is widely used in industrial operations, primarily in the synthetic organic chemicals industry. In addition, phosgene is produced by photochemical degradation of chlorinated hydrocarbons (e.g., trichloroethylene) emitted from various sources. Although phosgene is acutely toxic, its effects at low levels (i.e., 1 ppbv and below) are unknown. Nonetheless, its emission into and/or formation in ambient air is of potential concern.

4.2 The conventional method for phosgene has utilized a colorimetric procedure involving reaction with 4,4'-nitrobenzyl pyridine in diethyl phthalate. This method cannot detect phosgene levels below 10 ppbv and is subject to numerous interferences. The method described herein is more sensitive (0.1 ppbv detection limit) and is believed to be more selective due to the chromatographic separation step. However, the method needs to be more rigorously tested for interferences before its degree of selectivity can be firmly established.

5. Definitions

Definitions used in this document and in any user-prepared SOPs should be consistent with ASTM D1356 (3). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 There are very few interferences in the method, although this aspect of the method needs to be more thoroughly investigated. Ambient levels of nitrogen oxides, ozone, water vapor, and SO_2 are known not to interfere. Chloroformates can cause interferences by reacting with the aniline to form urea, which produces a peak that overlies the carbanilide peak in the HPLC trace. Presence of chloroformates should be documented before use of this method. However, the inclusion of a HPLC step overcomes most potential interferences from other organic compounds. High concentrations of acidic materials can cause precipitation of aniline salts in the impinger, thus reducing the amount of available reagent.

6.2 Purity of the aniline reagent is a critical factor, since traces of carbanilide have been found in reagent-grade aniline. This problem can be overcome by vacuum distillation of aniline in an all-glass apparatus.

7. Apparatus

7.1 Isocratic high performance liquid chromatography (HPLC) system consisting of a mobile-phase reservoir, a high-pressure pump, an injection valve, a Zorbax ODS or C-18 reverse-phase column, or equivalent (25 cm x 4.6 mm ID), a variable-wavelength UV detector operating at 254 nm, and a data system or strip-chart recorder (Figure 1).

7.2 Sampling system - capable of accurately and precisely sampling 100-1000 mL/minute of ambient air (Figure 2).

7.3 Stopwatch.

7.4 Friction-top metal can, e.g., one-gallon (paint can) - to hold sampling reagent and samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Analytical balance - 0.1 mg sensitivity.

7.8 Midget impingers - jet inlet type, 25 mL.

7.9 Nitrogen evaporator with heating block - for concentrating samples.

7.10 Suction filtration apparatus - for filtering HPLC mobile phase.

7.11 Volumetric flasks - 100 mL and 500 mL.

7.12 Pipettes - various sizes, 1-10 mL.

7.13 Helium purge line (optional) - for degassing HPLC mobile phase.

7.14 Erlenmeyer flask, 1-L - for preparing HPLC mobile phase.

7.15 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.16 Microliter syringe, 10-25 uL - for HPLC injection.

8. Reagents and Materials

8.1 Bottles, 16 oz. glass, with Teflon-lined screw cap - for storing sampling reagent.

8.2 Vials, 20 mL, with Teflon-lined screw cap - for holding samples and extracts.

8.3 Granular charcoal.

8.4 Acetonitrile, toluene, and methanol - distilled in glass or pesticide grade.

8.5 Aniline - 99+%, gold label from Aldrich Chemical Co., or equivalent.

8.6 Carbanilide - highest purity available; Aldrich Chemical Co., or equivalent.

8.7 Nitrogen, compressed gas cylinder - 99.99% purity for sample evaporation.

8.8 Polyester filters, 0.22 um - Nuclepore, or equiv.

9. Preparation of Sampling Reagent

9.1 Sampling reagent is prepared by placing 5.0 mL of aniline in a 250-mL volumetric flask and diluting to the mark with toluene. The flask is inverted 10-20 times to mix the reagent. The reagent is then placed in a clear 16-ounce bottle with a Teflon-lined screw cap. The reagent is refrigerated until use.

9.2 Before use, each batch of reagent is checked for purity by analyzing a 10-mL portion according to the procedure described in Section 11. If acceptable purity (<50 ng of carbanilide per 10 mL of reagent) is not obtained, the aniline or toluene is probably contaminated.

10. Sampling

10.1 The sampling apparatus is assembled and should be similar to that shown in Figure 2. EPA Method 6 uses essentially the same sampling system (5). All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven-dried before use.

10.2 Before sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. Flow rates greater than 1000 mL/minute ($\pm$2%) should not be used because impinger collection efficiency may decrease. Generally, calibration is accomplished using a soap bubble flow

meter or calibrated wet test meter connected to the flow exit, assuming that the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed-flow system downstream of the pump (3).

10.3 Ideally, a dry gas meter is included in the system to record total flow, if the flow rate is sufficient for its use. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling time exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

10.4 To collect an air sample, the midget impingers are loaded with 10 mL each of sampling reagent. The impingers are installed in the sampling system and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, sampling reagent batch number, and dry gas meter and pump identification numbers.

10.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed 50 L. If it does, the operator must use a second impinger.

10.6 At the end of the sampling period, the parameters listed in Section 10.4 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

10.7 Immediately after sampling, the impinger is removed from the sampling system. The contents of the impinger are emptied into a clean 20-mL glass vial with a Teflon-lined screw cap. The impinger is then rinsed with 2-3 mL of toluene and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can and refrigerated until analysis.

10.8 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 \cdots Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2 \ldots Q_N$ = flow rates determined at the beginning, end, and intermediate points during sampling.

N = number of points averaged.

10.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1)Q_A}{1000}$$

where

V_m = total sample volume (L) at measured temperature and pressure.

T_2 = stop time.

T_1 = start time.

$T_1 - T_2$ = total sampling time (minutes).

Q_a = average flow rate (mL/minute).

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples are returned to the laboratory in 20-ml screw-capped vials and refrigerated in charcoal containing cans until analysis.

11.1.2 The sample vial is placed in an aluminum heating block maintained at 60°C and a gentle stream of pure nitrogen gas is directed across the sample.

11.1.3 When the sample reaches complete dryness, the vial is removed from the heating block, capped, and cooled to near room temperature. A 1-mL volume of HPLC mobile phase (50/50 acetonitrile/water) is placed in the vial. The vial is then capped and gently shaken to dissolve the residue.

11.1.4 The concentrated sample is then refrigerated until HPLC analysis, as described in Section 11.2.

11.2 HPLC Analysis

11.2.1 The HPLC system is assembled and calibrated as described in Section 12. The operating parameters are as follows:

Column:	C-18 RP
Mobile Phase:	30% acetonitrile/70% distilled water
Detector:	ultraviolet, operating at 254 nm
Flow Rate:	1 mL/min

Before each analysis, the detector baseline is checked to ensure stable operation.

11.2.2 A 25-uL aliquot of the sample, dissolved in HPLC mobile phase, is drawn into a clean HPLC injection syringe. The sample injection loop is loaded and an injection is made. The data system is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorder.

11.2.3 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with mobile phase in preparation for the next sample analysis.

11.2.4 After elution of carbanilide, data acquisition is terminated and the component concentrations are calculated as described in Section 13.

11.2.5 Once a stable baseline is achieved, the system can be used for further sample analyses as described above.

11.2.6 If the concentration of carbanilide exceeds the linear range of the instruments, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.2.7 If the retention time is not duplicated, as determined by the calibration curve, you may increase or decrease the acetonitrile/water ratio to obtain the correct elution time, as specified in Figure 4. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio.

11.2.8 If a dirty column causes improper detection of carbanilide, you may reactivate the column by reverse solvent flushing utilizing the following sequence: water, methanol, acetonitrile, dichloromethane, hexane, acetonitrile, then 50/50 acetonitrile in water.

12. HPLC Assembly and Calibration

12.1 The HPLC system is assembled and operated according to the parameters outlined in Section 11.2.1. An example of a typical chromatogram oabtained using the above parameters is shown in Figure 4.

12.2 The mobile phase is prepared by mixing 500 mL of acetonitrile and 500 mL of reagent water. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon suction filtration. A constant back pressure restrictor (50 psi) or short length (6-12 inches) of 0.01-inch I.D. Teflon tubing should be placed after the detector to eliminate further mobile phase outgassing.

12.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis and the detector output is displayed on a strip-chart recorder or similar output device at a sensitivity of ca 0.008 absorbance units full scale (AUFS). Once a stable baseline is achieved, the system is ready for calibration.

12.4 Carbanilide standards are prepared in HPLC mobile phase. A concentrated stock solution of 100 mg/L is prepared by dissolving 10 mg of carbanilide in 100 mL of mobile phase. This solution is used to prepare calibration standards containing concentrations of 0.05-5 mg/L.

12.5 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. All calibration runs are performed as described for sample analyses in Section 11. Using the UV detector, a linear response range (Figures 5a through 5e) of approximately 0.1 to 10 mg/L should be achieved for a 25-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 6. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained.

12.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for ambient air, but at least 10 times the detection limit, should be chosen for daily calibration. The response for carbanilide should be within 10% day to day. If greater variability is observed, more frequent calibration may be required to ensure that valid results are obtained or a new calibration curve must be developed from fresh standards.

12.7 The response for carbanilide in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_C = \frac{C_C \times V_I}{R_C}$$

where

RF_C = response factor (usually area counts) for carbanilide in nanograms injected/response unit.

C_C = concentration (mg/L) of carbanilide in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_C = response (area counts) for carbanilide in calibration standard.

13. Calculations

13.1 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e., under ambient conditions). The value should be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.

V_m = total sample volume (L) under ambient conditions, calculated as in Section 10.9 or from dry gas meter reading.

P_A = ambient pressure (mm Hg).

T_A = ambient temperature (°C).

13.2 The concentration of carbanilide is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times \frac{V_E}{V_I}$$

where

W_d = total quantity of carbanilide (ug) in the sample.
RF_c = response factor calculated in Section 12.7.
R_d = response (area counts or other response units) for carbanilide in sample extract.
V_E = final volume (mL) of sample extract.
V_I = volume (uL) of extract injected into the HPLC system.

13.3 The concentration of phosgene in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times \frac{99}{212} \times 1000$$

where

C_A = concentration of phosgene (ng/L)in the original sample.
W_d = total quantity of carbanilide (ug) in sample.
V_m = total sample volume (L) under ambient conditions.
V_c = total sample volume (L) at 25 ^{o}C and 760 mm Hg.
$\frac{99}{212}$ = the molecular weights (g/mole) of phosgene and carbanilide are 99 and 212 g/mole, respectively.

13.4 The phosgene concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times \frac{24.4}{99}$$

where

C_A (ng/L) is calculated using V_S.

14. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

14.1 Standard Operating Procedures (SOPs).

14.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration, and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling reagent and samples; 3) assembly, calibration, and operation of the HPLC system with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

14.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

14.2 HPLC System Performance

14.2.1 The general appearance of the HPLC chromatogram should be similar to that illustrated in Figure 4.

14.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner:

A solution of carbanilide corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 7, and should be between 0.8 and 1.8.

14.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \frac{t_r}{W_{1/2}}$$

where

N = column efficiency (theoretical plates).
t_r = retention time (seconds) of carbanilide.
$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

14.2.4 Precision of response for replicate HPLC injections should be $\pm$10% or less, day to day, for calibration standards. Precision of retention times should be $\pm$2%, on a given day.

14.3 Process Blanks

14.3.1 Before use, a 10-mL aliquot of each batch of sampling reagent should be analyzed as described in Section 11. The blank should contain less than 50 ng of carbanilide per 10-mL aliquot.

14.3.2 At least one field blank or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in Section 14.3.1 should be met for process blanks.

14.4 Method Precision and Recovery

14.4.1 Analysis of replicate samples indicates that a precision of ±15-20% relative standard deviation can be readily achieved (see Table 1). Each laboratory should collect parallel samples periodically (at least one for each batch of samples) to document its precision in conducting the method.

14.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

14.4.3 Before using the method in the field, each laboratory must confirm the performance of the method under its particular conditions. Since static, dilute, gas phase standards of phosgene are unstable, a dynamic flow/permeation tub system should be assembled as described in the literature[1]. ASTM Method D 3609[3] should be used as the protocol for operating such a system.

14.4.4 Once a suitable dynamic flow/permeation tube system has been constructed, a series of three samples from the outlet gas stream (60 L) should be sampled at three different spike levels (achieved by adjusting the air flow through the permeation chamber). Precision and recovery data comparable to those shown in Table 1 should be achieved.

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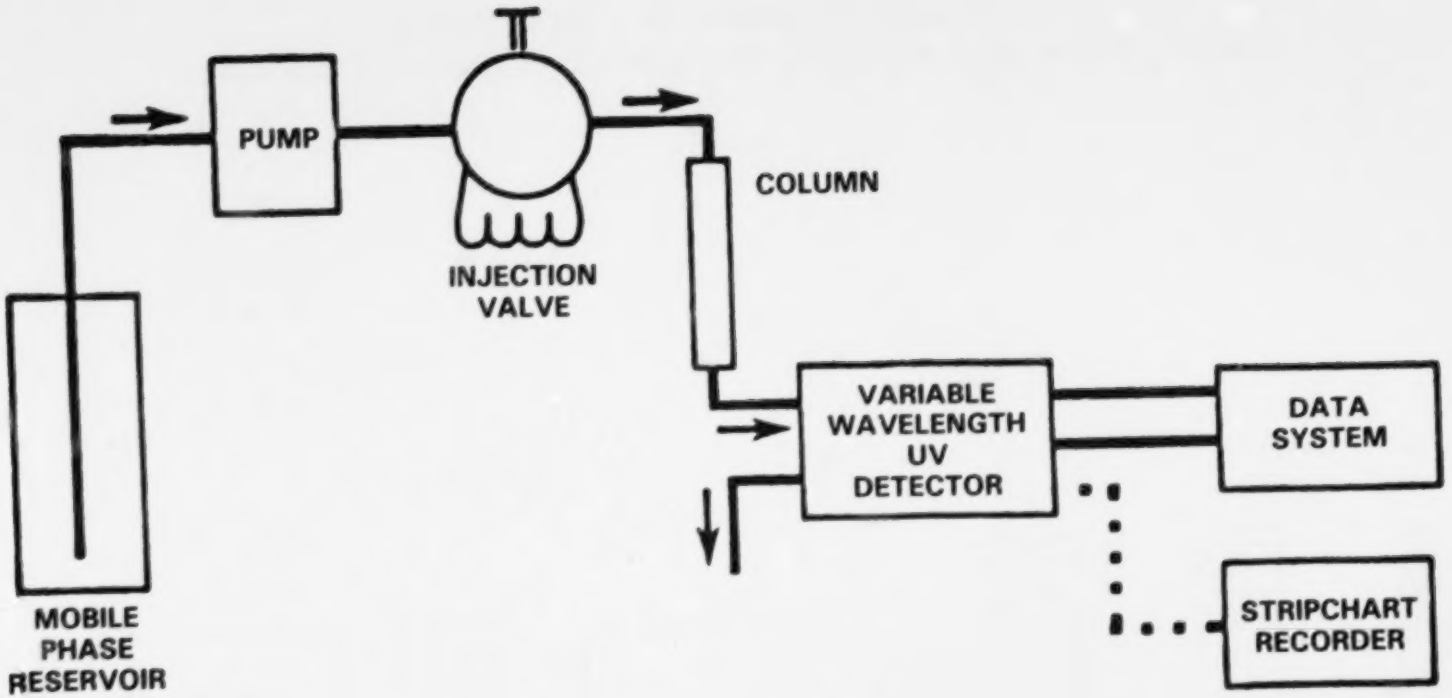
3. Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania, 1983.

4. Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

5. "Method 6 Determination of SO_2 Emissions from Stationary Sources," Federal Register, Vol. 42., No. 160, August, 1977.



T06-17

FIGURE 1. TYPICAL HPLC SYSTEM

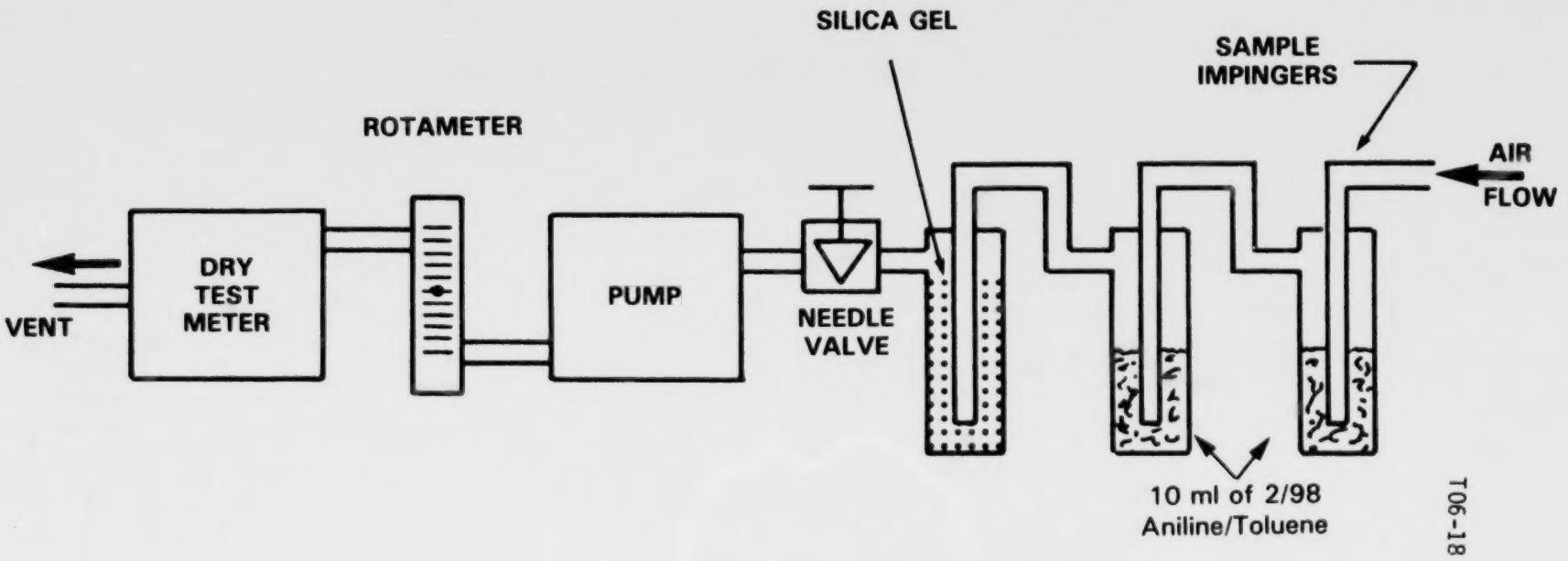


FIGURE 2. TYPICAL SAMPLING SYSTEM FOR MONITORING PHOSGENE IN AMBIENT AIR

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATES(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

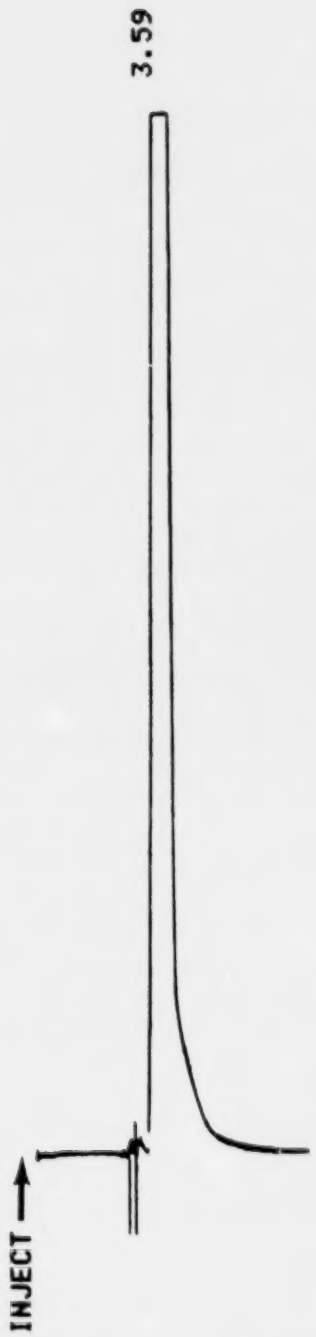
V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_ \text{ L}$$

* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 3. TYPICAL SAMPLING DATA FORM



OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes

AUG. 22, 1986 15:25:17 CHART 0.50 CM/MIN
RUN #50 CALC #0
COLUMN SOLVENT OPR ID: 3

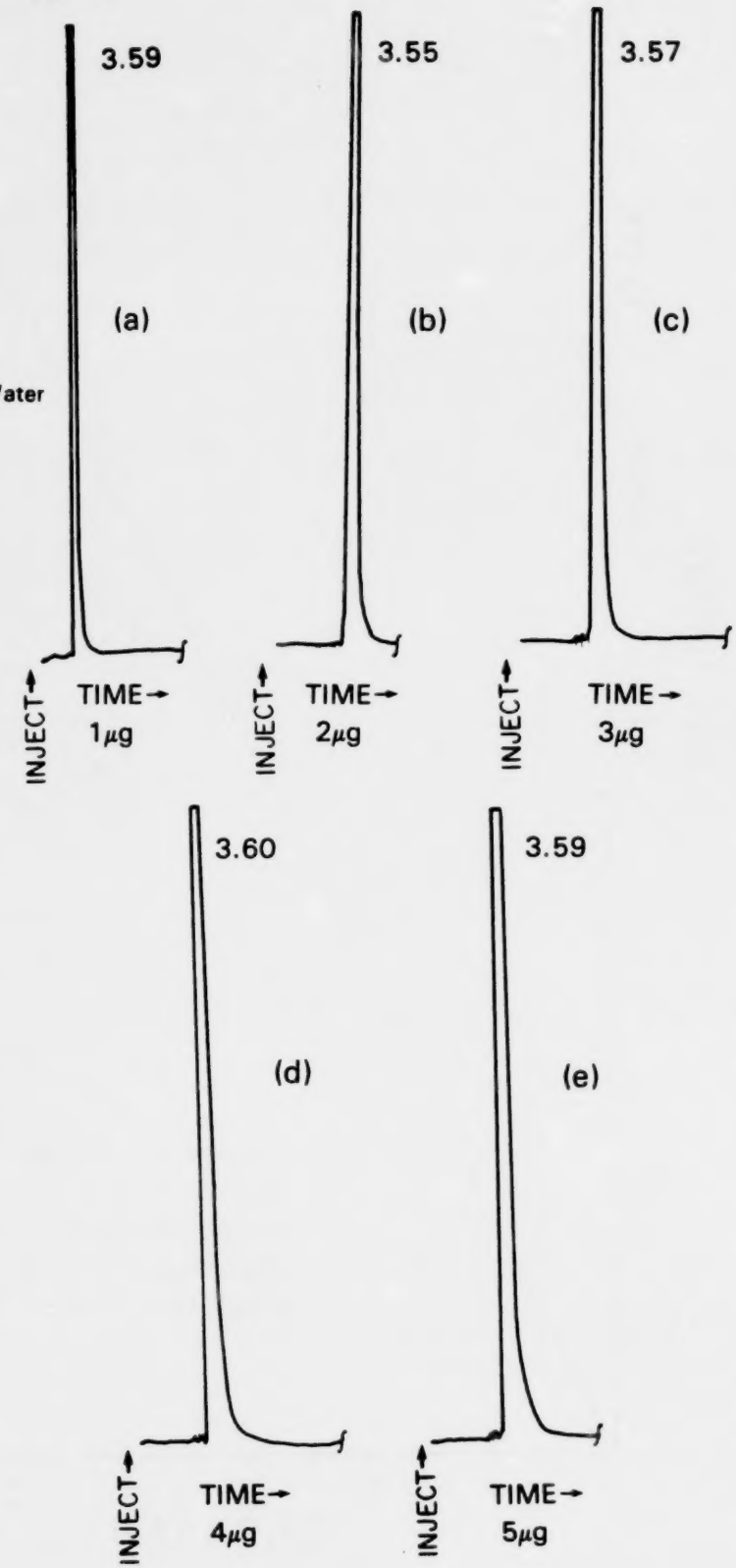
EXTERNAL STANDARD QUANTITATION

PEAK #	AMOUNT	RT	EXP RT	AREA	RF
	2.75300	2.74		2753 L	0.000000E0
	10020.20000	3.59		10020345 L	0.000000E0
TOTAL	10023.00000				

FIGURE 4. CHROMATOGRAM FOR 3 ppbv OF PHOSGENE SPIKED INTO CLEAN AIR

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Distilled Water
Detector: Ultra violet operating at 254 nm
Flow Rate: 1 ml/min
Retention Time: 3.59 minutes



CONC	AREA COUNTS
1μg	2126577
2μg	4243289
3μg	6312128
4μg	8373790
5μg	10020345

FIGURE 5a-5e. HPLC CHROMATOGRAM OF VARYING CARBANILIDE CONCENTRATIONS

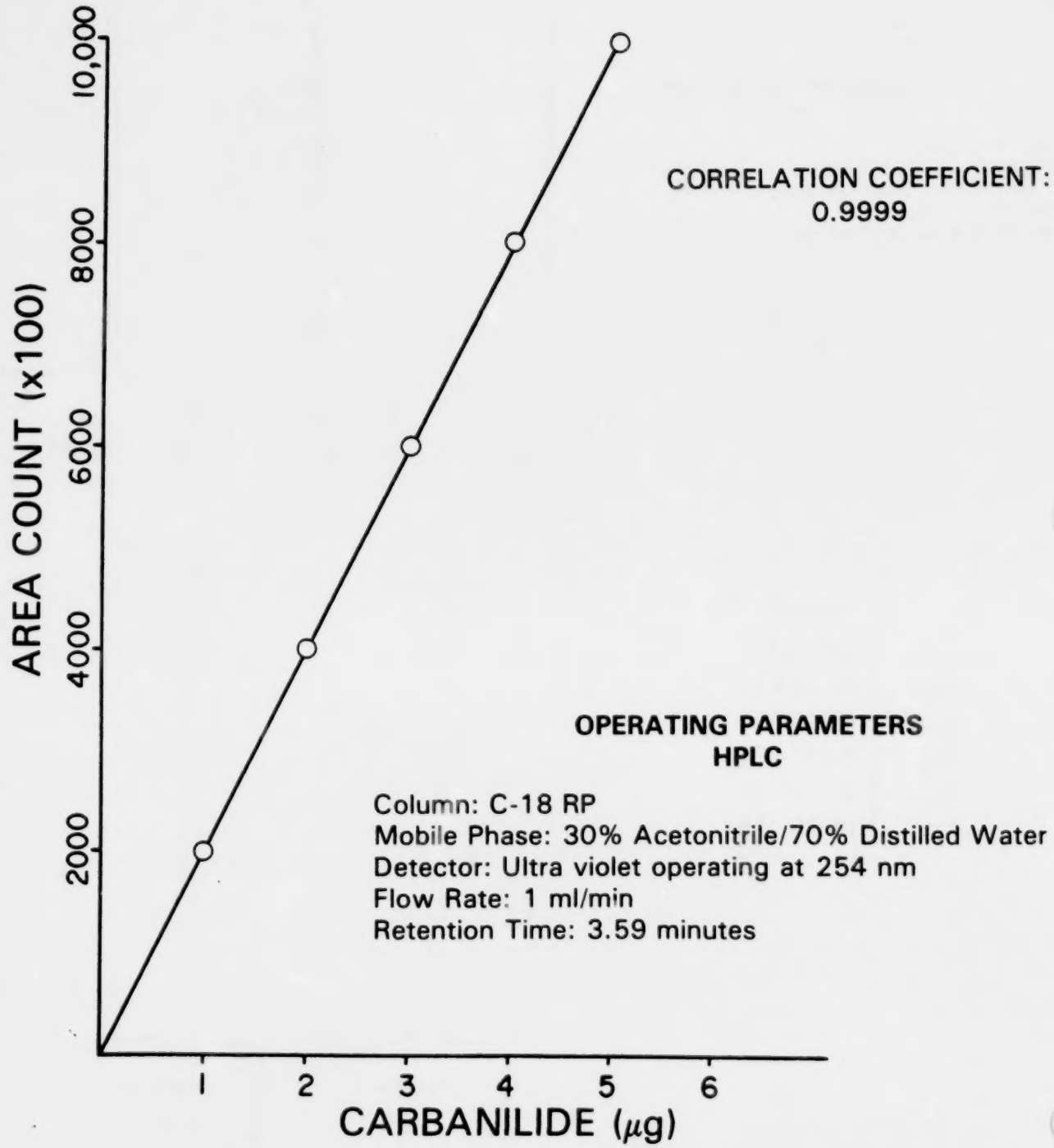
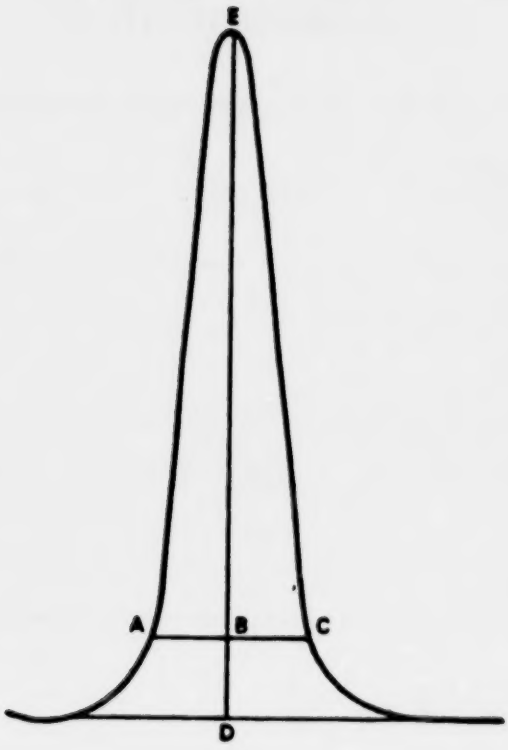


FIGURE 6. CALIBRATION CURVE FOR CARBANILINE



$$\text{Asymmetry Factor} = \frac{BC}{AB}$$

Example Calculation:

Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 7. PEAK ASYMMETRY CALCULATION

TABLE 1: PRECISION AND RECOVERY DATA FOR PHOSGENE IN CLEAN AIR

Phosgene Concentration, ppbv	Recovery, %	Standard Deviation
0.034	63	13
0.22	87	14
3.0	99	3
4.3	109	12
20	99	14
200	96	7

Revision 1.0
September, 1986

METHOD TO7

METHOD FOR THE DETERMINATION OF N-NITROSODIMETHYLAMINE IN AMBIENT AIR USING GAS CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of N-nitrosodimethylamine (NDMA) in ambient air. Although the method, as described, employs gas chromatography/mass spectrometry (GC/MS), other detection systems are allowed.

1.2 Although additional documentation of the performance of this method is required, a detection limit of better than 1 ug/m^3 is achievable using GC/MS (1,2). Alternate, selective GC detection systems such as a thermal energy analyzer (2), a thermionic nitrogen-selective detector (3), or a Hall Electrolytic conductivity detector (4) may prove to be more sensitive and selective in some instances.

2. Applicable Documents

2.1 ASTM Standards
D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis (5)

2.2 Other Documents
Ambient air studies (1,2)
U.S. EPA Technical Assistance Document (6)

3. Summary of Method

3.1 Ambient air is drawn through a Thermosorb/N adsorbent cartridge at a rate of approximately 2 L per minute for an appropriate period of time. Breakthrough has been shown

not to be a problem with total sampling volumes of 300 L (i.e., 150 minutes at 2 L per minute). The selection of Thermosorb/N absorbent over Tenax GC, was due, in part, to recent laboratory studies indicating artifact formation on Tenax from the presence of oxides of nitrogen in the sample matrix.

3.2 In the laboratory, the cartridges are pre-eluted with 5 mL of dichloromethane (in the same direction as sample flow) to remove interferences. Residual dichloromethane is removed by purging the cartridges with air in the same direction. The cartridges are then eluted, in the reverse direction, with 2 mL of acetone. This eluate is collected in a screw-capped vial and refrigerated until analysis.

3.3 NDMA is determined by GC/MS using a Carbowax 20M capillary column. NDMA is quantified from the response of the m/e 74 molecular ion using an external standard calibration method.

4. Significance

4.1 Nitrosamines, including NDMA, are suspected human carcinogens. These compounds may be present in ambient air as a result of direct emission (e.g., from tire manufacturing) or from atmospheric reactions between secondary or tertiary amines and NO_x.

4.2 Several papers (1,2,4) have been published describing analytical approaches for NDMA determination. The purpose of this document is to combine the attractive features of these methods into one standardized method. At the present time, this method has not been validated in its final form, and, therefore, one must use caution when employing it for specific applications.

5. Definitions

Definitions used in this document and in any user-prepared SOPs should be consistent with ASTM D1356(5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

Compounds having retention times similar to NDMA, and yielding detectable m/e 74 ion fragments, may interfere in the method. The inclusion of a pre-elution step in the sample desorption procedure minimizes the number of interferences. Alternative GC columns and conditions may be required to overcome interferences in unique situations.

7. Apparatus

7.1 GC/MS System - capable of temperature-programmed, fused-silica capillary column operation. Unit mass resolution or better to 300 amu. Capable of full scan and selected ion monitoring with a scan rate of 0.8 second/scan or better.

7.2 Sampling system - capable of accurately and precisely sampling 100-2000 mL/minute of ambient air. (See Figure 1.) The dry test meter may not be accurate at flows below 500 mL/minute; in such cases it should be replaced by recorded flow readings at the start, finish, and hourly during the collection. See Section 9.4.

7.3 Stopwatch.

7.4 Friction top metal can, e.g., one-gallon (paint can) - to hold clean cartridges and samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Glass syringe - 5 mL with Luer® fitting.

7.8 Volumetric flasks - 2 mL, 10 mL, and 100 mL.

7.9 Glass syringe - 10 uL for GC injection.

8. Reagents and Materials

8.1 Thermosorb/N - Available from Thermedics Inc., 470 Wildwood St., P.O.Box 2999, Woburn, Mass., 01888-1799, or equivalent.

8.2 Dichloromethane - Pesticide quality, or equivalent.

8.3 Helium - Ultrapure compressed gas (99.9999%).

8.4 Perfluorotributylamine (FC-43) - for GC/MS calibration.

8.5 Chemical Standards - NDMA solutions. Available from various chemical supply houses. Caution: NDMA is a suspected human carcinogen. Handle in accordance with OSHA regulations.

8.6 Granular activated charcoal - for preventing contamination of cartridges during storage.

8.7 Glass jar, 4 oz - to hold cartridges.

8.8 Glass vial - 1 dram, with Teflon®-lined screw cap.

8.9 Luer® fittings - to connect cartridges to sampling system.

8.10 Acetone- Reagent grade.

9. Sampling

9.1 Cartridges (Thermosorb/N) are purchased prepacked from Thermedics Inc. These cartridges are 1.5 cm ID x 2 cm long polyethylene tubes with Luer®-type fittings on each end. The adsorbent is held in place with 100-mesh stainless steel screens at each end. The cartridges are used as received and are discarded after use. At least one cartridge from each production lot should be used as a blank to check for contamination. The cartridges are stored in screw-capped glass jars (with Luer® style caps), and placed in a charcoal-containing metal can when not in use.

9.2 The sampling system may employ either a mass flow controller or a dry test meter. (See Figure 1.) For purposes of discussion, the following procedure assumes the use of a dry test meter.

9.3 Before sample collection, the entire assembly (including a "dummy" sampling cartridge) is installed and the flow rate is checked at a value near the desired rate. In general, flow rates of 100-2000 mL/minute should be employed. The flow rate should be adjusted so that no more than 300 L of air is collected over the desired sampling period. Generally, calibration is accomplished using a soap bubble flow meter or

calibrated wet test meter connected to the flow exit, assuming the system is sealed. ASTM Method 3686 describes an appropriate calibration scheme not requiring a sealed flow system downstream of the pump.

9.4 Ideally, a dry gas meter is included in the system to record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

9.5 To collect an air sample, a new Thermosorb/N cartridge is removed from the glass jar and connected to the sampling system using a Luer® adapter fitting. The glass jar is sealed for later use. The following parameters are recorded on the data sheet (see Figure 2 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, cartridge batch number, and dry gas meter and pump identification numbers.

9.6 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total flow should not exceed 300 L.

9.7 At the end of the sampling period, the parameters listed in Section 9.5 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

9.8 Immediately after sampling, the cartridge is removed from the sampling system, capped, and placed back in the 4-oz

glass jar. The jar is then capped, sealed with Teflon® tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can until analysis.

9.9 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \cdots Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2, \ldots . Q_N$ = flow rates determined at beginning, end, and immediate points during sampling.

N = number of points averaged.

9.10 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

where

V_m = total sample volume (L) at measured temperature and pressure.

T_2 = stop time.

T_1 = start time.

$T_2 - T_1$ = sampling time (minutes).

9.11 The total volume (V_S) at standard conditions, 25°C and 760 mm Hg, is calculated from the following equation:

$$V_S = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where V_S = total sample volume (L) at standard conditions of 25° C and 760 mm Hg.

V_m = total sample volume (L) at measured temperature and pressure.

P_A = average barometric pressure (mm Hg).

t_A = average ambient temperature (°C).

10. Sample Desorption

10.1 Samples are returned to the laboratory and prepared for analysis within one week of collection.

10.2 Using a glass syringe, the samples are pre-eluted to remove potential interferences by passing 5 mL of dichloromethane through the cartridge, in the same direction as sample flow. This operation should be conducted over approximately a 2-minute period. Excess solvent is expelled by injecting 5 mL of air through the cartridge, again using the glass syringe.

10.3 The NDMA is then desorbed passing 2 mL of acetone through the cartridge, in the direction opposite to sample flow, using a glass syringe. A flow rate of approximately 0.5 mL/minute is employed and the eluate is collected in a 2-mL volumetric flask.

10.4 Desorption is halted once the volumetric flask is filled to the mark. The sample is then transferred to a 1-dram vial having a Teflon®-lined screw cap and refrigerated until analysis. The vial is wrapped with aluminum foil to prevent photolytic decomposition of the NDMA.

11. GC/MS Analysis

Although a variety of GC detectors can be used for NDMA determination, the following procedure assumes the use of GC/MS in the selected ion monitoring (SIM) mode.

11.1 Instrument Setup

11.1.1 Considerable variation in instrument configuration is expected from one laboratory to another. Therefore, each laboratory must be responsible for verifying that its particular system yields satisfactory results. The GC/MS system must be capable of accommodating a fused-silica capillary column, which can be inserted directly into the ion source. The system must be capable of acquiring and processing data in the selected ion monitoring mode.

11.1.2 Although alternative column systems can be used, a 0.2 mm I.D. x 50 m Carbowax 20M fused-silica column (Hewlett-Packard Part No. 19091-60150, or equivalent) is recommended. After installation, a helium carrier gas flow of 2 mL per minute is established and the column is conditioned at 250°C for 16 hours. The injector and GC/MS transfer line temperatures should also be set at 250°C.

11.1.3 The MS and data system are set up according to manufacturer's specifications. Electron impact ionization (70 eV) should be employed. Once the entire GC/MS system is set up, it is calibrated as described in Section 11.2. The user should prepare a detailed standard operating procedure (SOP) describing this process for the particular instrument being used.

11.2 Instrument Calibration

11.2.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user-prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens, voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 1 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these values must be repeatable on a day-to-day basis.

11.2.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system, the user should set the SIM monitoring parameters (i.e., mass centroid and window to be monitored) by injecting a moderatley high level standard solution (100 ug/mL) of NDMA onto the GC/MS in the full scan mode. The scan range should be 40 to 200 amu at a rate of 0.5 to 0.8 scans/second. The nominal mass 42, 43, and 74 amu ions are to be used for SIM monitoring, with the 74 amu ion employed for NDMA quantification.

11.2.3 Before injection of NDMA standards, the GC oven temperature is stabilized at 45°C. The filament and electron multiplier voltage are turned off. A 2-uL aliquot of an appropriate NDMA standard, dissolved in acetone, is injected onto the GC/MS system using the splitless injection technique. Concentrated NDMA standards can be purchased from chemical supply houses. The standards are diluted to the appropriate concentration with acetone. CAUTION: NDMA is a suspected carcinogen and must be handled according to OSHA regulations. After five minutes, the electron multiplier and filament are turned on, data acquisition is initiated, and the oven temperature is programmed to 250°C at a rate of 16°C/minute. After elution of the NDMA peak from the GC/MS (Figure 3), the data acquisition process can be halted and data processing initiated.

11.2.4 Once the appropriate SIM parameters have been established, as described in Section 11.2.2, the instrument is calibrated by analyzing a range of NDMA standards using the SIM prodecure. If necessary, the electron multiplier voltage or amplifier gain can be adjusted to give the desired sensitivity for standards bracketing the range of interest. A calibration curve of m/e 74 ion intensity versus quantity of NDMA injected is constructed and used to calculate NDMA concentration in the samples.

11.3 Sample Analysis

11.3.1 The sample analysis process is the same as that described in Section 11.2.3 for calibration standards. Samples should be handled so as to minimize exposure to light.

11.3.2 If a peak is observed for NDMA (within ±6 seconds of the expected retention time), the areas (integrated ion intensities) for m/e 42, 43, and 74 are calculated. The area of the m/e 74 peak is used to calculate NDMA concentration. The ratios of m/e 42/74 and 43/74 ion intensities are used to determine the certainty of the NDMA identification. Ideally, these ratios should be within ±20% of the ratios for an NDMA standard in order to have confidence in the peak identification. Figure 4 illustrates the MS scan for N-nitrosodimethylamine.

12. Calculations

12.1 Calibration Response Factors

12.1.1 Data from calibration standards are used to calculate a response factor for NDMA. Ideally, the process involves analysis of at least three calibration levels of NDMA during a given day and determination of the response factor (area/ng injected) from the linear least squares fit of a plot of nanograms injected versus area (for the m/e 74 ion). In general, quantities of NDMA greater than 1000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 If substantial nonlinearity is present in the calibration curve, a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where

Y = peak area

X = quantity of NDMA (ng)

A, B, and C are coefficients in the equation

12.2 NDMA Concentration

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$Y_A = A + BX_A + CX_A^2$$

where

Y_A is the area of the m/e 74 ion for the sample injection.

X_A is the calculated quantity of NDMA (ng) on the sample cartridge.

A, B, and C are the coefficients calculated from the calibration curve described in Section 12.1.2.

12.2.2 If instrumental response is essentially linear over the concentration range of interest, a linear equation (C=0 in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$C_A = \frac{X_A}{V_S}$$

where

C_A is the calculated concentration of analyte (ng/L).

V_S and X_A are as previously defined in Sections 9.11 and 12.2.1, respectively.

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 User should generate SOPs describing the following activites in their laboratory: 1) assembly, calibration, and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of Thermosorb/N cartridges and samples; 3) assembly, calibration, and operation of the GC/MS system with make and model of equipment used; and 4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 Sample Collection

13.2.1 During each sampling event, at least one clean cartridge will accompany the samples to the field and back to the laboratory, having been placed in the sampler but without sampling air, to serve as a field blank. The average amount of material found on the field blank cartridges may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25% of the sample amount, data for that component must be identified as suspect.

13.2.2 During each sampling event, at least one set of parallel samples (two or more samples collected simultaneously) should be collected. If agreement

between parallel samples is not generally within ±25%, the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points).

13.2.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 10% of the amount of NDMA found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater.

13.2.4 NDMA recovery for spiked cartridges (using a solution-spiking technique) should be determined before initial use of the method on real samples. Currently available information indicates that a recovery of 75% or greater should be achieved.

13.3 GC/MS Analysis

13.3.1 Performance criteria for MS tuning and mass standardization are discussed in Section 11.2 and Table 1. Additional criteria can be used by the laboratory, if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GC/MS system.

13.3.2 Chromatographic efficiency should be evaluated daily by the injection of NDMA calibration standards. The NDMA peak should be plotted on an expanded time scale so that its width at 10% of the peak height can be calculated, as shown in Figure 5. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 5) should be between 0.8 and 2.0.

13.3.3 The detection limit for NDMA is calculated from the data obtained for calibration standards. The detection limit is defined as

$$DL = A + 3.3S$$

where

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.2.

S is the standard deviation of replicate determinations of the lowest-level standard (at least three such determinations are required). The lowest-level standard should yield a signal-to-noise ratio (from the total ion current response) of approximately 5.

13.3.4 Replicate GC/MS analysis of NDMA standards and/or sample extracts should be conducted on a daily basis. A precision of $\pm$15% RSD or better should be achieved.

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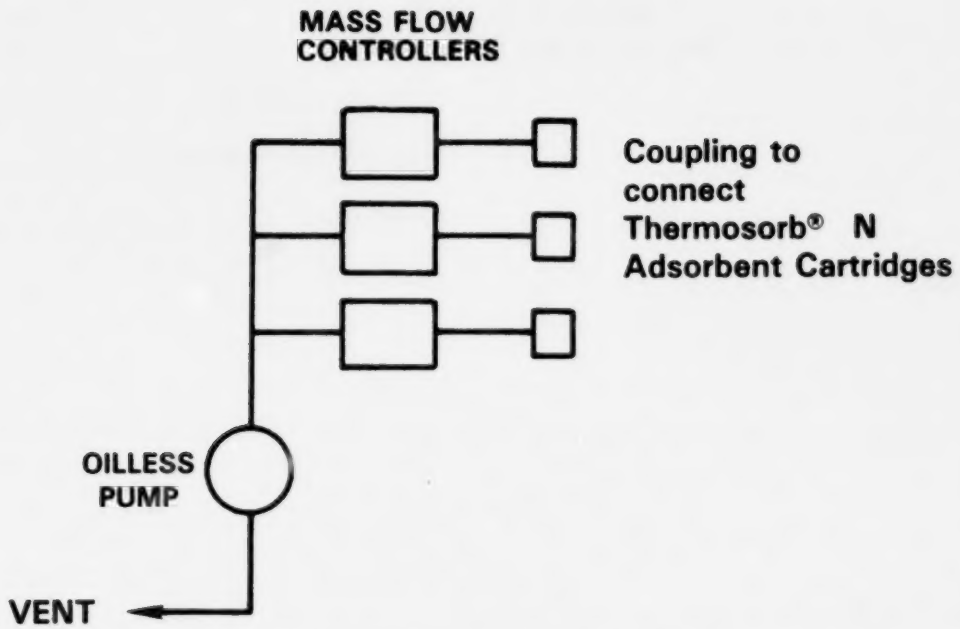
(3) "EPA Method 607 - Nitrosamines," Federal Register, 49, 43313-43319, October 26, 1984.

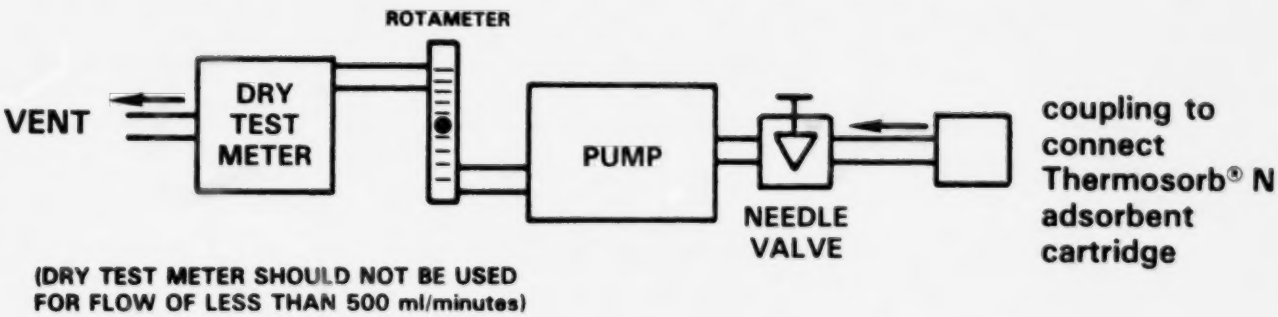
(4) Anderson, R. J., "Nitrogen-Selective Detection in Gas Chromatography," Tracor Inc. Applications Note 79-3, Austin, Texas.

(5) Annual Book of ASTM Standards, Part 11.03, "Atmospheric Analysis," American Society for Testing and Materials, Philadelphia, Pennsylvania.

(6) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.



(a) MASS FLOW CONTROL


ROTAMETER
VENT
DRY TEST METER
PUMP
NEEDLE VALVE
coupling to connect Thermosorb® N adsorbent cartridge
(DRY TEST METER SHOULD NOT BE USED FOR FLOW OF LESS THAN 500 ml/minutes)

(b) NEEDLE VALVE/DRY TEST METER

FIGURE 1. TYPICAL SAMPLING SYSTEM CONFIGURATION

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATES(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_ \text{ L}$$

* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 2. EXAMPLE SAMPLING DATA SHEET

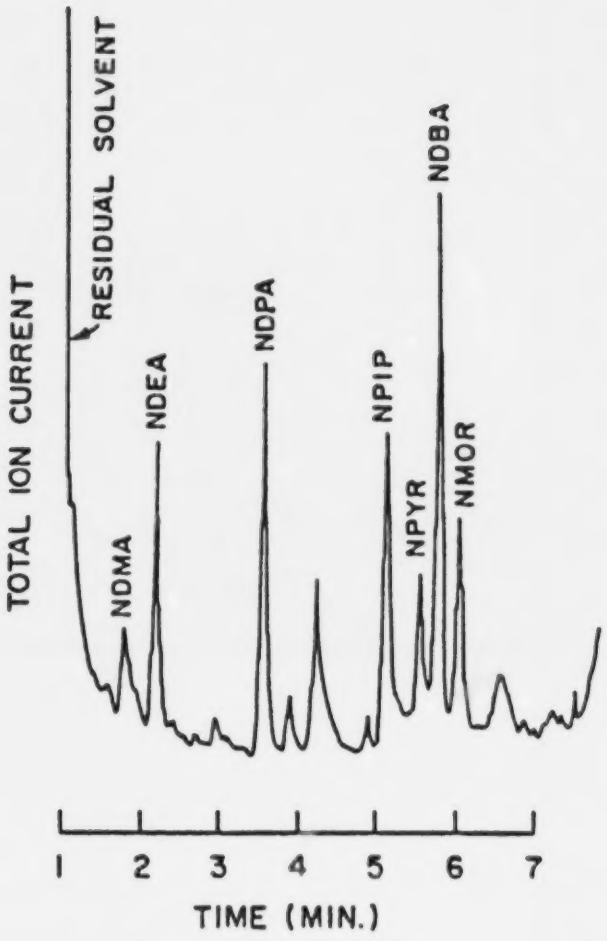


FIGURE 3. TOTAL ION CURRENT CHROMATOGRAM RESULTING FROM INJECTION OF 15 μL SAMPLE OF NDMA STANDARD (10 NG/μL IN ETHANOL).

$C_2H_6N_2O$

Methanamine, *N*—methyl—*N*—nitroso—

Me $_2$ NNO

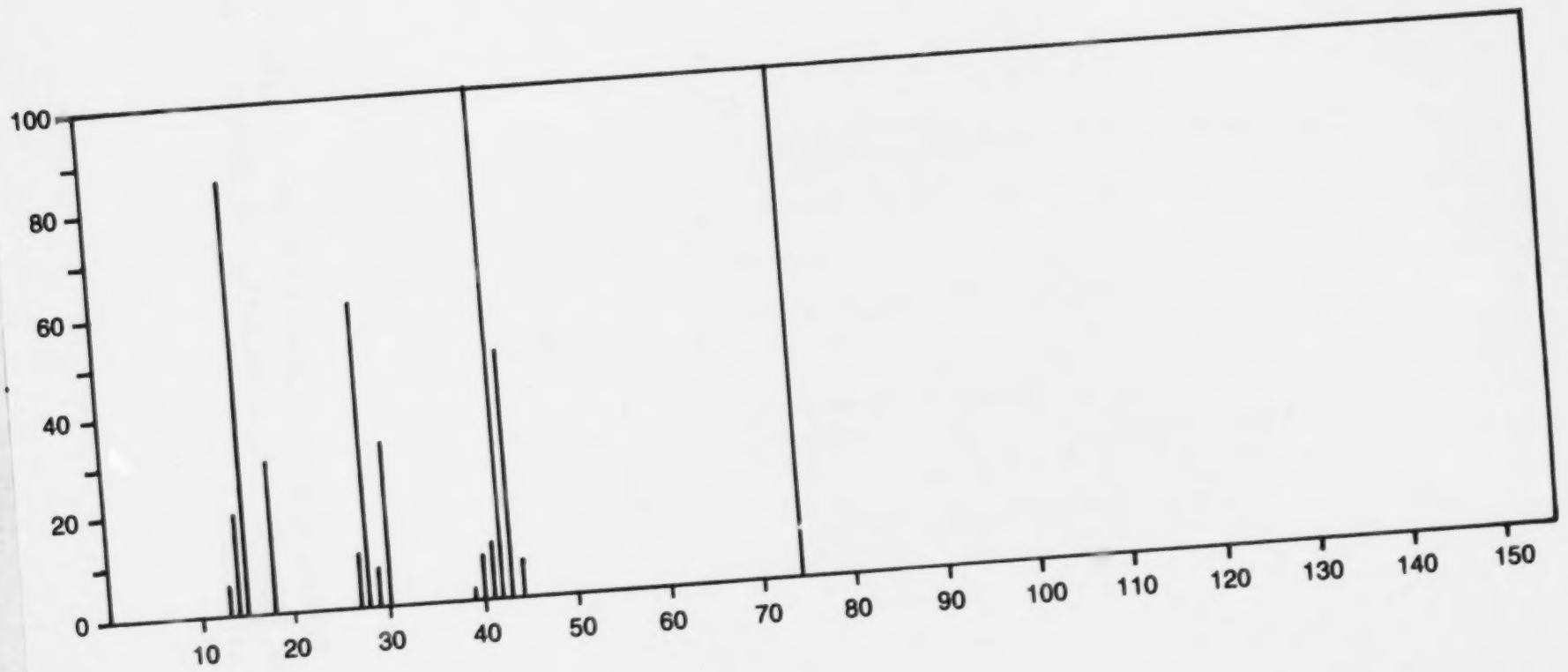
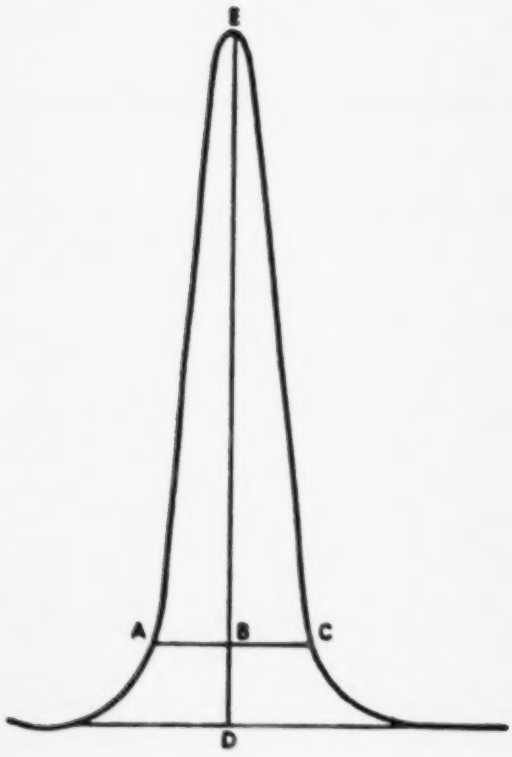


FIGURE 4. MASS SPECTROSCOPY SCAN (10 TO 150 AMV) OF NDMA AT A RATE OF 0.5 TO 0.8 SCANS/SECOND



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:
Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 5. PEAK ASYMMETRY CALCULATION

TABLE 1: SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION ABUNDANCES FROM FC-43 MASS CALIBRATION

M/E	% Relative Abundance
51	1.8 ± 0.5
69	100
100	12.0 ± 1.5
119	12.0 ± 1.5
131	35.0 ± 3.5
169	3.0 ± 0.4
219	24.0 ± 2.5
264	3.7 ± 0.4
314	0.25 ± 0.1

Revision 1.0
September, 1986

METHOD TO8

METHOD FOR THE DETERMINATION OF PHENOL AND METHYLPHENOLS (CRESOLS) IN AMBIENT AIR USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. Scope

1.1 This document describes a method for determination of phenol and methylphenols (cresols) in ambient air. With careful attention to reagent purity and other factors, the method can detect these compounds at the 1-5 ppbv level.

1.2 The method as written has not been rigorously evaluated. The approach is a composite of several existing methods (1-3). The choice of HPLC detection system will be dependent on the requirements of the individual user. However, the UV detection procedure is considered to be most generally useful for relatively clean samples.

2. Applicable Documents

2.1 ASTM Standards

D1356 - Definitions of Terms Related to Atmospheric Sampling and Analysis(4).

2.2 Other Documents

U.S. EPA Technical Assistance Document (5).

3. Summary of Method

3.1 Ambient air is drawn through two midget impingers, each containing 15 mL of 0.1 N NaOH. The phenols are trapped as phenolates.

3.2 The impinger solutions are placed in a vial with a Teflon®-lined screw cap and returned to the laboratory for

analysis. The solution is cooled in an ice bath and adjusted to pH <4 by addition of 1 mL of 5% v/v sulfuric acid. The sample is adjusted to a final volume of 25 mL with distilled water.

3.3 The phenols are determined using reverse-phase HPLC with either ultraviolet (UV) absorption detection at 274 nm, electrochemical detection, or fluorescence detection. In general, the UV detection approach should be used for relatively clean samples.

4. Significance

4.1 Phenols are emitted into the atmosphere from chemical operations and various combustion sources. Many of these compounds are acutely toxic, and their determination in ambient air is required in order to assess human health impacts.

4.2 Conventional methods for phenols have generally employed colorimetric or gas chromatographic techniques with relatively large detection limits. The method described here reduces the detection limit through use of HPLC.

5. Definitions

Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D1356 (5). All abbreviations and symbols are defined within this document at the point of use.

6. Interferences

6.1 Compounds having the same retention times as the compounds of interest will interfere in the method. Such interferences can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions) or detectors. Additionally, the phenolic compounds of interest in this method may be oxidized during sampling. Validation experiments may be required to show that the four target compounds are not substantially degraded.

6.2 If interferences are suspected in a "dirty" sample, preliminary cleanup steps may be required to identify interfering compounds by recording infrared spectrophotometry followed by specific ion-exchange column chromatography. Likewise, overlapping HPLC peaks may be resolved by increasing/decreasing component concentration of the mobile phase.

6.3 All reagents must be checked for contamination before use.

7. Apparatus

7.1 Isocratic HPLC system consisting of a mobile-phase reservoir, a high-pressure pump, an injection valve, a Zorbax ODS or C-18 reverse-phase column, or equivalent (25 cm x 4.6 mm ID), a variable-wavelength UV detector operating at 274 nm, and a data system or strip-chart recorder (Figure 1). Amperometric (electrochemical) or fluorescence detectors may also be employed.

7.2 Sampling system - capable of accurately and precisely sampling 100-1000 mL/minute of ambient air (Figure 2).

7.3 Stopwatch.

7.4 Friction-top metal can, e.g., one-gallon (paint can) - to hold samples.

7.5 Thermometer - to record ambient temperature.

7.6 Barometer (optional).

7.7 Analytical balance - 0.1 mg sensitivity.

7.8 Midget impingers - jet inlet type, 25-mL.

7.9 Suction filtration apparatus - for filtering HPLC mobile phase.

7.10 Volumetric flasks - 100 mL and 500 mL.

7.11 Pipettes - various sizes, 1-10 mL.

7.12 Helium purge line (optional) - for degassing HPLC mobile phase.

7.13 Erlenmeyer flask, 1 L - for preparing HPLC mobile phase.

7.14 Graduated cylinder, 1 L - for preparing HPLC mobile phase.

7.15 Microliter syringe, 100-250 uL - for HPLC injection.

8. Reagents and Materials

8.1 Bottles, 10 oz, glass, with Teflon®-lined screw cap - for storing sampling reagent.

8.2 Vials, 25 mL, with Teflon®-lined screw cap - for holding samples.

8.3 Disposable pipettes and bulbs.

8.4 Granular charcoal.

8.5 Methanol - distilled in glass or pesticide grade.

8.6 Sodium hydroxide - analytical reagent grade.

8.7 Sulfuric acid - analytical reagent grade.

8.8 Reagent water - purified by ion exchange and carbon filtration, or distillation.

8.9 Polyester filters, 0.22 um - Nuclepore, or equivalent.

8.10 Phenol, 2-methyl-, 3-methyl-, and 4-methylphenol - neat standards (99+ % purity) for instrument calibration.

8.11 Sampling reagent, 0.1 N NaOH. Dissolve 4.0 grams of NaOH in reagent water and dilute to a final volume of 1 L. Store in a glass bottle with Teflon®-lined cap.

8.12 Sulfuric acid, 5% v/v. Slowly add 5 mL of concentrated sulfuric acid to 95 mL of reagent water.

8.13 Acetate buffer, 0.1M, pH 4.8 - Dissolve 5.8 mL of glacial acetic acid and 13.6 grams of sodium acetate trihydrate in 1 L of reagent water.

8.14 Acetonitrile - spectroscopic grade.

8.15 Glacial acetic acid - analytical reagent grade.

8.16 Sodium acetate trihydrate - analytical reagent grade.

9. Sampling

9.1 The sampling apparatus is assembled and should be similar to that shown in Figure 2. EPA Federal Reference Method 6 uses essentially the same sampling system (6). All glassware (e.g., impingers, sampling bottles, etc.) must be thoroughly rinsed with methanol and oven-dried before use.

9.2 Before sample collection, the entire assembly (including empty sample impingers) is installed and the flow rate checked at a value near the desired rate. In general, flow rates of 100-1000 mL/minute are useful. Flow rates greater than 1000 mL/minute should not be used because impinger collection

efficiency may decrease. Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the entire system is sealed. ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed-flow system downstream of the pump (4).

9.3 Ideally, a dry gas meter is included in the system to record total flow, if the flow rate is sufficient for its use. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling time exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Ideally, a rotameter should be included to allow observation of the flow rate without interruption of the sampling process.

9.4 To collect an air sample, two clean midget impingers are loaded with 15 mL of 0.1 N NaOH each and sample flow is started. The following parameters are recorded on the data sheet (see Figure 3 for an example): date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, 0.1 N NaOH reagent batch number, and dry gas meter and pump identification numbers.

9.5 The sampler is allowed to operate for the desired period, with periodic recording of the variables listed above. The total volume should not exceed 80 L. The operator must ensure that at least 5 mL of reagent remains in the impinger at the end of the sampling interval. (Note: for high ambient temperatures, lower sampling volumes may be required.)

9.6 At the end of the sampling period, the parameters listed in Section 9.4 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and

end of the sampling period differ by more than 15%, the sample should be discarded.

9.7 Immediately after sampling, the impinger is removed from the sampling system. The contents of the impinger are emptied into a clean 25-mL glass vial with a Teflon®-lined screw-cap. The impinger is then rinsed with 5 mL of reagent water and the rinse solution is added to the vial. The vial is then capped, sealed with Teflon® tape, and placed in a friction-top can containing 1-2 inches of granular charcoal. The samples are stored in the can and refrigerated until analysis. No degradation has been observed if the time between refrigration and analysis is less than 48 hours.

9.8 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \cdots Q_N}{N}$$

where

Q_A = average flow rate (mL/minute).

$Q_1, Q_2, \ldots . Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling.

N = number of points averaged.

9.9 The total flow is then calculated using the following equation:

$$V_m = \frac{(T_2 - T_1) \times Q_A}{1000}$$

where

V_m = total volume (L) sampled at measured temperature and pressure.
T_2 = stop time.
T_1 = start time.
T_2-T_1 = total sampling time (minutes).
Q_A = average flow rate (ml/minute).

9.10 The volume of air sampled is often reported uncorrected for atmospheric conditions (i.e., under ambient conditions). However, the value should be adjusted to standard conditions (25°C and 760 mm pressure) using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + T_A}$$

where

V_s = total sample volume (L) at 25°C and 760 mm Hg pressure.
V_m = total sample volume (L) under ambient conditions. Calculated as in Section 9.9 or from dry gas meter reading.
P_A = ambient pressure (mm Hg).
T_A = ambient temperature (°C).

10. Sample Analysis

10.1 Sample Preparation

10.1.1 The samples are returned to the laboratory in 25-mL screw-capped vials. The contents of each vial are transferred to a 25-mL volumetric flask. A 1-mL volume of 5% sulfuric acid is added and the final volume is adjusted to 25 mL with reagent water.

10.1.2 The solution is thoroughly mixed and then placed in a 25-ml screw-capped vial for storage (refrigerated) until HPLC analysis.

10.2 HPLC Analysis

10.2.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column:	C-18 RP	
Mobile Phase:	30% acetonitrile/70% acetate buffer solution	
Detector:	ultraviolet, operating at 274 nm	
Flow Rate:	0.3 mL/minute	
Retention Time:	phenol - 9.4 minutes	Individual
	o-cresol - 12.5 minutes	Individual
	m-cresol - 11.5 minutes	Individual
	p-cresol - 11.9 minutes	Individual
	phenol - 9.4 minutes	Combined
	o-cresol - 12.8 minutes	Combined
	m/p-cresol - 11.9 minutes	Combined

Before each analysis, the detector baseline is checked to ensure stable operation.

10.2.2 A 100-uL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (50 uL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection and the point of injection is marked on the strip-chart recorder.

10.2.3 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with water in preparation for the next sample analysis.

10.2.4 After elution of the last component of interest, data acquisition is terminated and the component concentrations are calculated as described in Section 12.

10.2.5 Phenols have been successfully separated from cresols utilizing HPLC with the above operating parameters. However, meta- and para-cresols have not been successfully separated. Figure 4 illustrates a typical chromatogram.

10.2.6 After a stable baseline is achieved, the system can be used for further sample analyses as described above.

10.2.7 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

10.2.8 If the retention time is not duplicated, as determined by the calibration curve, you may increase or decrease the acetonitrile/water ratio to obtain the correct elution time, as specified in Figure 4. If the elution time is long, increase the ratio; if it is too short, decrease the ratio.

11.0 HPLC Assembly and Calibration

11.1 The HPLC system is assembled and operated according to Section 10.2.1.

11.2 The HPLC mobile phase is prepared by mixing 300 mL of acetonitrile and 750 mL of acetate buffer, pH 4.8. This mixture is filtered through a 0.22-um polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/minute) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (50 psi) or short length (6-12 inches) of 0.01-inch I.D. Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 0.3 mL/minute and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis and the detector output is displayed on a strip-chart recorder or similar output device. UV detection at 274 nm is generally preferred. Alternatively, fluorescence detection with 274-nm excitation at 298-nm emission (2), or electrochemical detection at 0.9 volts (glassy carbon electrode versus Ag/AgCl) (3) may be used. Once a stable baseline is achieved, the system is ready for calibration.

11.4 Calibration standards are prepared in HPLC mobile phase from the neat materials. Individual stock solutions of 100 mg/L are prepared by dissolving 10 mg of solid derivative in 100 mL of mobile phase. These individual solutions are used to prepare calibration standards containing all of the phenols and cresols of interest at concentrations spanning the range of interest.

11.5 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass injected. Figures 5a through 5e illustrate HPLC response to various phenol concentrations (1 mL/minute flow rate). All calibration runs are performed as described for sample analyses in Section 10. Using the UV detector, a linear response range of approximately 0.05 to 10 mg/L should be achieved for 50-uL injection volumes. The results may be used to prepare a calibration curve, as illustrated in Figure 6 for phenols. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (concentration versus area response) is obtained. The retention times for each analyte should agree within 2%.

11.6 Once linear response has been documented, an intermediate concentration standard near the anticipated levels for each component, but at least 10 times the detection limit, should be chosen for daily calibration. The response for the various components should be within 10% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.

11.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation:

$$RF_c = \frac{C_c \times V_I}{R_c}$$

where

RF_c = response factor (usually area counts) for the component of interest in nanograms injected/response unit.

C_c = concentration (mg/L) of analyte in the daily calibration standard.

V_I = volume (uL) of calibration standard injected.

R_c = response (area counts) for analyte in the calibration standard.

12. Calculations

12.1 The concentration of each compound is calculated for each sample using the following equation:

$$W_d = RF_c \times R_d \times \frac{V_E}{V_I} \times \frac{V_D}{V_A}$$

where

W_d = total quantity of analyte (ug) in the sample.

RF_c = response factor calculated in Section 11.6.

R_d = response (area counts or other response units) for analyte in sample extract.

V_E = final volume (mL) of sample extract.

V_I = volume of extract (uL) injected onto the HPLC system.

V_D = redilution volume (if sample was rediluted).

V_A = aliquot used for redilution (if sample was rediluted).

12.2 The concentration of analyte in the original sample is calculated from the following equation:

$$C_A = \frac{W_d}{V_m \text{ (or } V_s)} \times 1000$$

where

C_A = concentration of analyte (ng/L) in the original sample.
W_d = total quantity of analyte (ug) in sample.
V_m = total sample volume (L) under ambient conditions.
V_s = total sample volume (L) at 25 ^{o}C and 760 mm Hg.

12.3 The analyte concentrations can be converted to ppbv using the following equation:

$$C_A \text{ (ppbv)} = C_A \text{ (ng/L)} \times \frac{24.4}{MW_A}$$

where

C_A (ng/L) is calculated using V_s.
MW_A = molecular weight of analyte.

13. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 Users should generate SOPs describing the following activities in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling reagent and samples; (3) assembly, calibration,

and operation of the HPLC system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC chromatogram should be similar to that illustrated in Figure 4.

13.2.2 The HPLC system efficiency and peak asymmetry factor should be determined in the following manner: A solution of phenol corresponding to at least 20 times the detection limit should be injected with the recorder chart sensitivity and speed set to yield a peak approximately 75% of full scale and 1 cm wide at half height. The peak asymmetry factor is determined as shown in Figure 7, and should be betweeen 0.8 and 1.8.

13.2.3 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54\left(\frac{t_r}{W_{1/2}}\right)^2$$

where

N = column efficiency (theoretical plates).
t_r = retention time (seconds) of analyte.
$W_{1/2}$ = width of component peak at half height (seconds).

A column efficiency of >5,000 theoretical plates should be obtained.

13.2.4 Precision of response for replicate HPLC injections should be $\pm$10% or less, day to day, for calibration standards. Precision of retention times should be $\pm$2%, on a given day.

13.3 Process Blanks

13.3.1 Before use, a 15-mL aliquot of each batch of 0.1 N NaOH reagent should be analyzed as described in Section 10. In general, analyte levels equivalent to <5 ng/L in an 80-L sample should be achieved.

13.3.2 At least one field blank, or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified percentage of blanks is obtained for a given number of field samples. The field blank is treated identically to the samples except that no air is drawn through the reagent. The same performance criteria described in Section 13.3.1 should be met for process blanks.

13.4 Method Precision and Accuracy

13.4.1 At least one duplicate sample, or 10% of the field samples, whichever is larger, should be collected during each sampling episode. Precision for field replication should be $\pm$20% or better.

13.4.2 Precision for replicate HPLC injections should be $\pm$10% or better, day to day, for calibration standards.

13.4.3 At least one spiked sample, or 10% of the field samples, whichever is larger, should be collected. The impinger solution is spiked with a known quantity of the compound of interest, prepared as a dilute water solution. A recovery of >80% should be achieved routinely.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 $\pm$10% and blank levels of <5 ng/L (using an 80-L sampling volume) should be achieved.

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(2) Ogan, K. and, Katz, E., "Liquid Chromatographic Separation of Alkylphenols with Fluorescence and Ultraviolet Detection," Anal. Chem., 53, 160-163 (1981).

(3) Shoup, R. E., and Mayer, G. S., "Determination of Environmental Phenols by Liquid Chromatography Electrochemistry," Anal. Chem., 54, 1164-1169 (1982).

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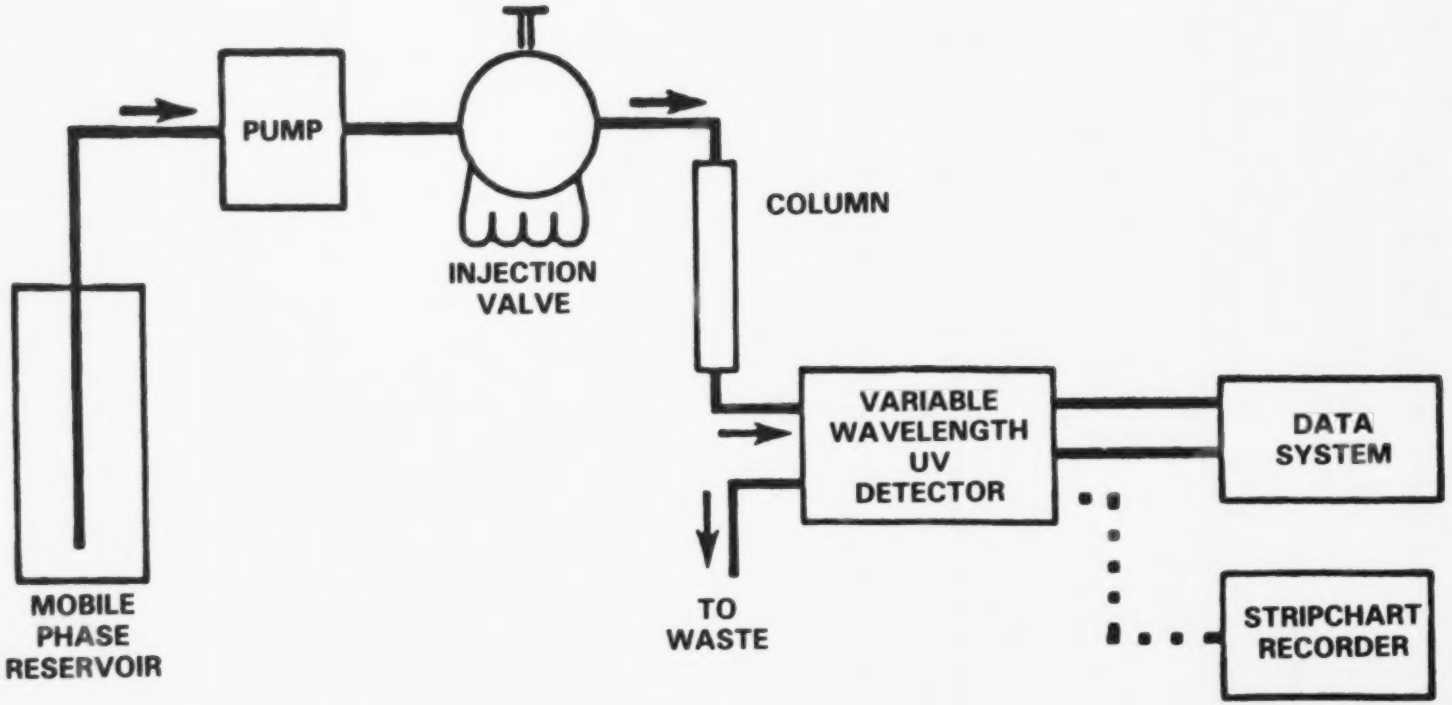
(5) Riggin, R. M., "Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air," EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1983.

(6) "Method 6 Determination of SO_2 Emissions from Stationary Sources," Federal Register, Vol. 42., No. 160, August, 1977.



T08-16

FIGURE 1. TYPICAL HPLC SYSTEM

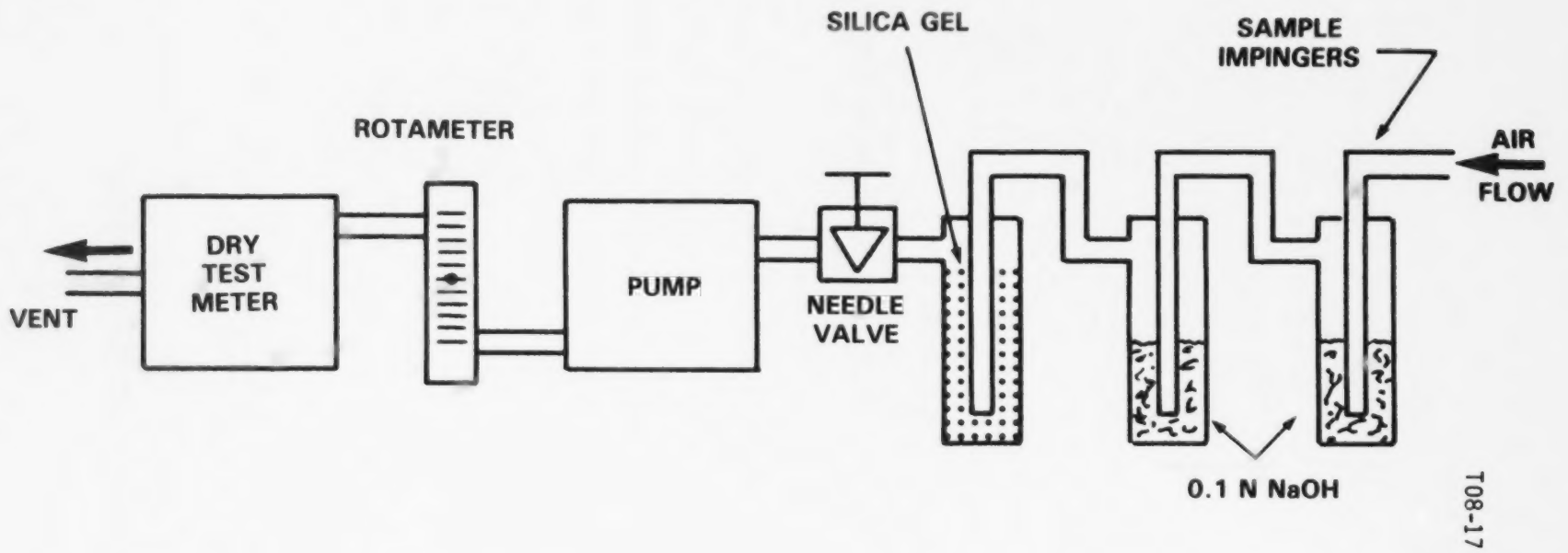


FIGURE 2. TYPICAL SAMPLING SYSTEM FOR MONITORING PHENOLS/CRESOLS IN AMBIENT AIR

SAMPLING DATA SHEET
(One Sample per Data Sheet)

PROJECT: _____ DATES(S) SAMPLED: _____

SITE: _____ TIME PERIOD SAMPLED: _____

LOCATION: _____ OPERATOR: _____

INSTRUMENT MODEL NO: _____ CALIBRATED BY: _____

PUMP SERIAL NO: _____

SAMPLING DATA

Sample Number: _____

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate,*Q mL/min	Ambient Temperature °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
1.							
2.							
3.							
4.							
N.							

Total Volume Data**

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L

$$= \frac{Q_1 + Q_2 + Q_3 \cdots Q_N}{N} \times \frac{1}{1000 \times (\text{Sampling Time in Minutes})} = \_\_\_\_\_ \text{ L}$$

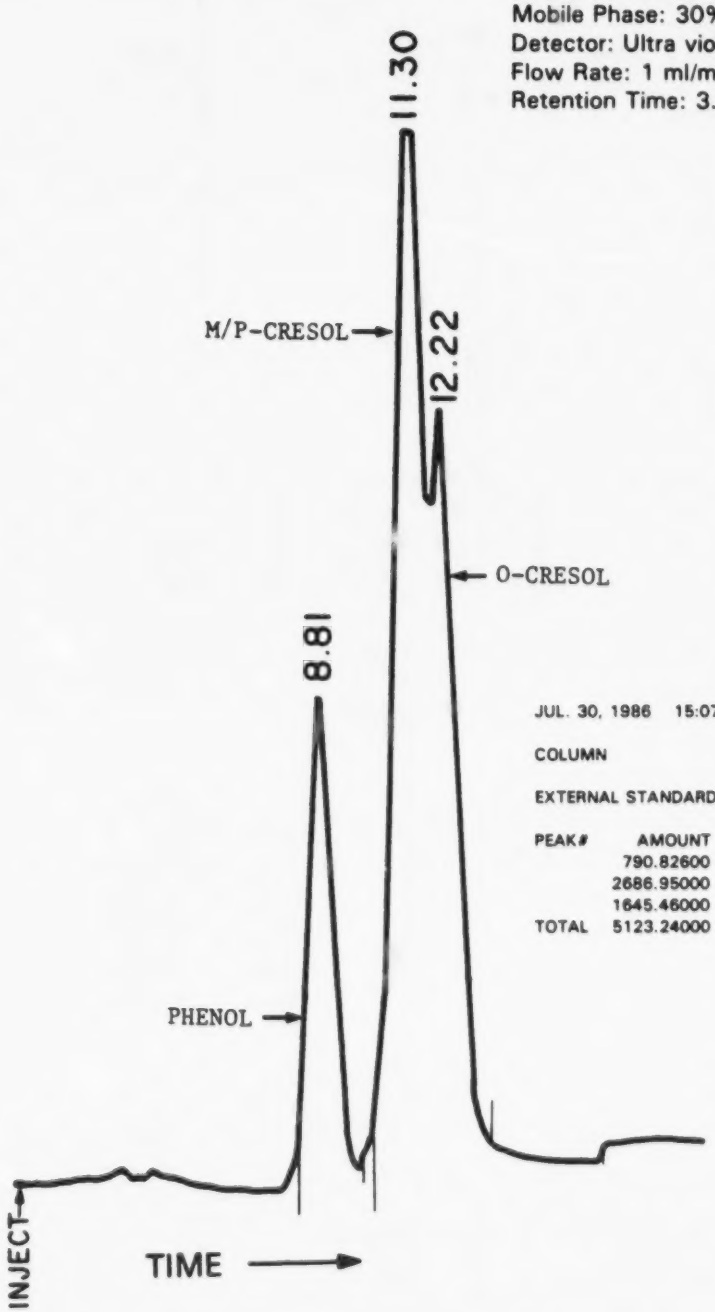
* Flow rate from rotameter or soap bubble calibrator (specify which).

** Use data from dry gas meter if available.

FIGURE 3. EXAMPLE SAMPLING DATA SHEET

OPERATING PARAMETERS
HPLC

Column: C-18 RP
Mobile Phase: 30% Acetonitrile/70% Acetate Buffer
Detector: Ultra violet operating at 274 nm
Flow Rate: 1 ml/min
Retention Time: 3.4 minutes

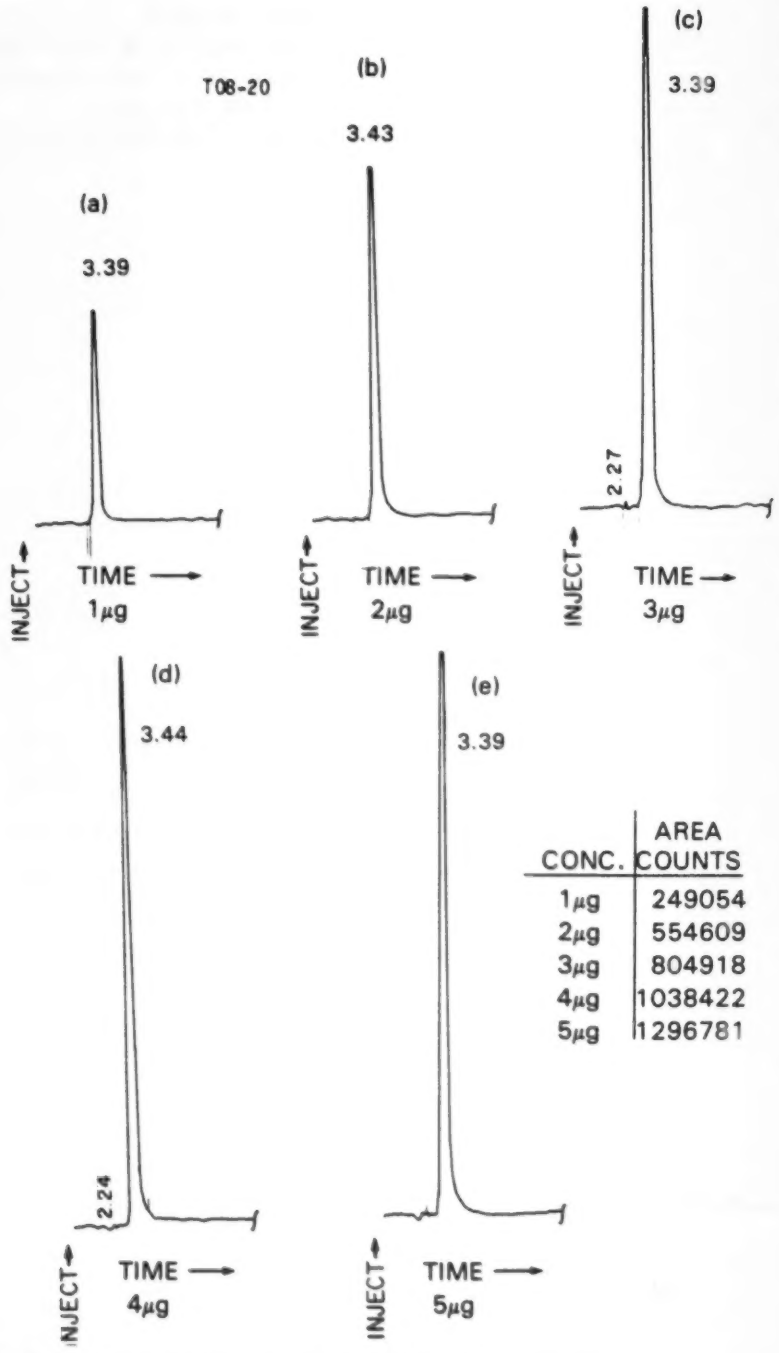


JUL. 30, 1986 15:07:17 CHART 0.50 CM/MIN
RUN #43 CALC #0
COLUMN SOLVENT OPR ID: 3

EXTERNAL STANDARD QUANTITATION

PEAK#	AMOUNT	RT	EXP RT	AREA	RF
	790.82600	8.81		790826 L	0.000000E0
	2686.95000	11.30		2686966 F	0.000000E0
	1645.46000	12.22		1645466 L	0.000000E0
TOTAL	5123.24000				

FIGURE 4. TYPICAL CHROMATOGRAM ILLUSTRATING SEPARATION OF PHENOLS/CRESOLS BY HPLC



CONC.	AREA COUNTS
1μg	249054
2μg	554609
3μg	804918
4μg	1038422
5μg	1296781

FIGURE 5a-5e. HPLC CHROMATOGRAM OF VARYING PHENOL CONCENTRATIONS

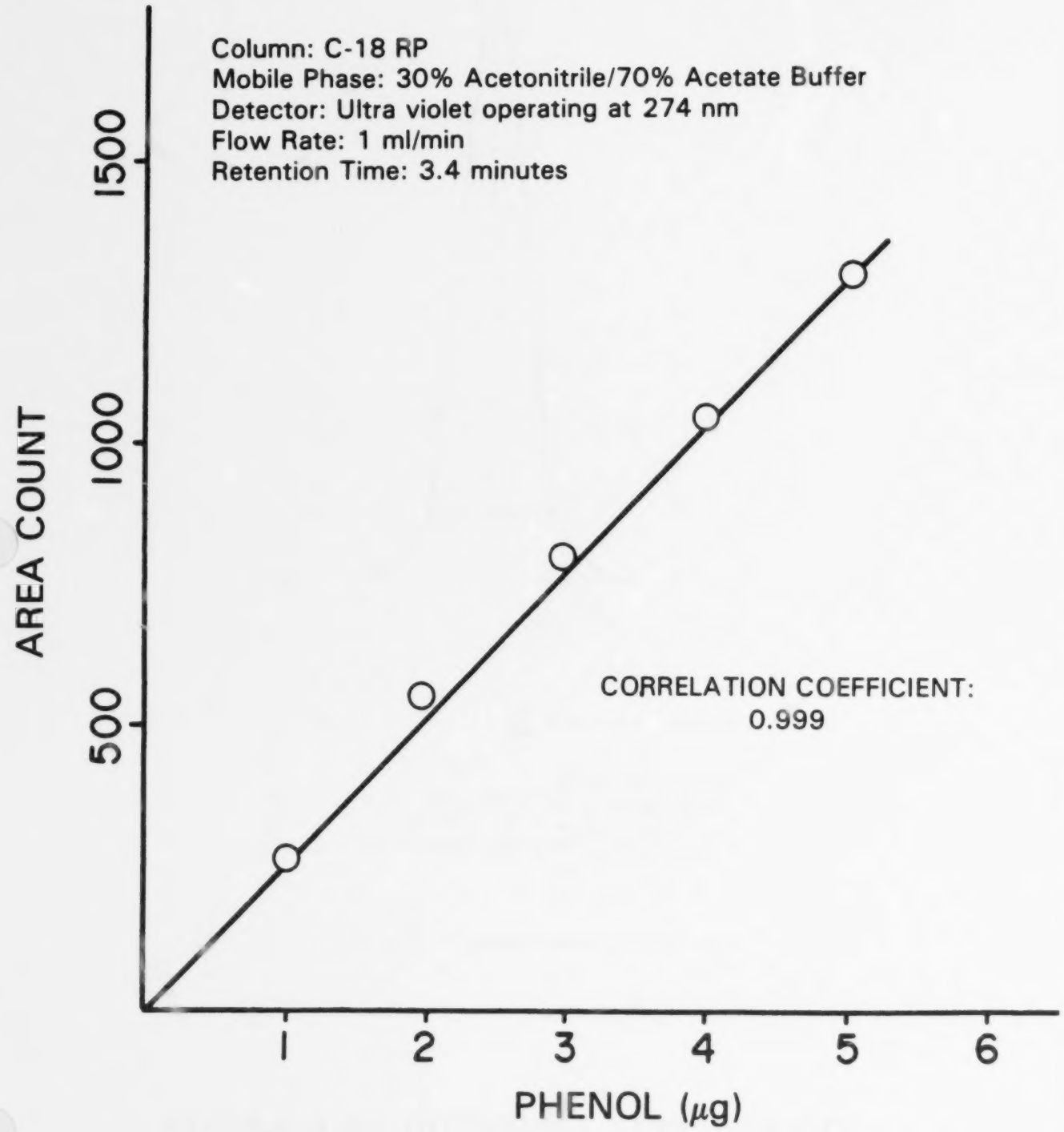
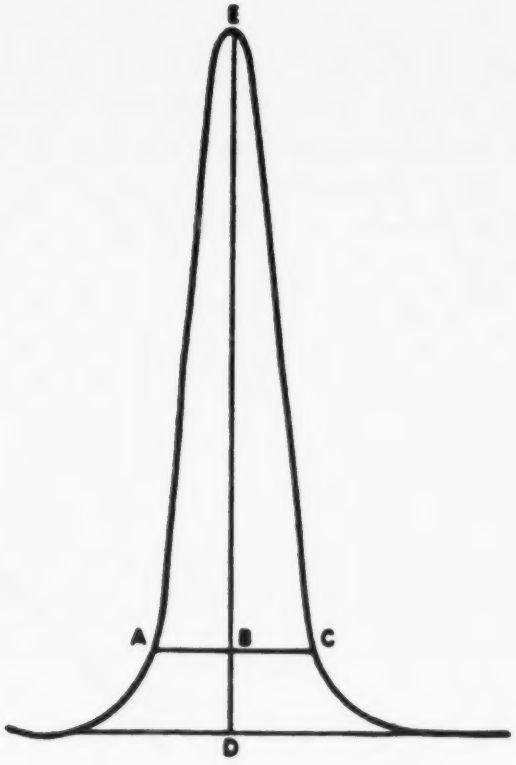


FIGURE 6. CALIBRATION CURVE FOR PHENOL



Asymmetry Factor = $\frac{BC}{AB}$

Example Calculation:
Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Asymmetry Factor = $\frac{12}{11}$ = 1.1

FIGURE 7. PEAK ASYMMETRY CALCULATION

Revision 1.0
September, 1986

METHOD TO9

METHOD FOR THE DETERMINATION OF POLYCHLORINATED DIBENZO-p-DIOXINS (PCDDs) IN AMBIENT AIR USING HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS SPECTROMETRY (HRGC/HRMS)

1. Scope

1.1 This document describes a method for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air. In particular, the following PCDDs have been evaluated in the laboratory utilizing this method:

- 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD)
- 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (1,2,3,4,7,8-H_xCDD)
- Octachlorodibenzo-p-dioxin (OCDD)
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

The method consists of sampling ambient air via an inlet filter followed by a cartridge (filled with polyurethane foam) and analysis of the sample using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Original laboratory studies have indicated that the use of polyurethane foam (PUF) or silica gel in the sampler will give equal efficiencies for retaining PCDD/PCDF isomers; i.e., the median retention efficiencies for the PCDD isomers ranged from 67 to 124 percent with PUF and from 47 to 133 percent with silica gel. Silica gel, however, produced lower levels of background interferences than PUF. The detection limits were, therefore, approximately four times lower for tetrachlorinated isomers and ten times lower for hexachlorinated isomers when using silica gel as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers. However, due to variable recovery and extensive cleanup required with silica gel, the method has been written using PUF as the adsorbent.

1.2 With careful attention to reagent purity and other factors, the method can detect PCDDs in filtered air at levels below 15 pg/m^3.

1.3 Average recoveries ranged from 68 percent to 140 percent in laboratory evaluations of the method sampling ultrapure filtered air. Percentage recoveries and sensitivities obtainable for ambient air samples have not been determined.

2. Applicable Documents

2.1 ASTM Standards

2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.

2.1.2 Method E260 - Recommended Practice for General Gas Chromatography Procedures.

2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.

2.2 EPA Documents

2.2.1 Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - "Ambient Air Specific Methods," Section 2.2 - "Reference Method for the Determination of Suspended Particulates in the Atmosphere," Revision 1, July, 1979, EPA-600/4-77-027A.

2.2.2. Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin by High Resolution Gas Chromatography-High Resolution Mass Spectrometry, U.S. Environmental Protection Agency, January, 1986, EPA-600/4-86-004.

2.2.3 Evaluation of an EPA High Volume Air Sampler for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans, undated report by Battelle under Contract 68-02-4127, Project Officers Robert G. Lewis and Nancy K. Wilson, U.S. Environmental Protection Agency, EMSL, Research Triangle Park, North Carolina.

2.2.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, April, 1984, 600/4-84-041.

2.2.5 Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, June, 1983, EPA-600/4-83-027.

2.3 Other Documents

2.3.1 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.

2.3.2 Chicago Air Quality: PCB Air Monitoring Plan, Phase 2, Illinois Environmental Protection Agency, Division of Air Pollution Control, April, 1986, IEPA/APC/86-011.

3. Summary of Method

3.1 Filters and adsorbent cartridges (containing PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.

3.2 Approximately 325 m^3 of ambient air is drawn through a cartridge on a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not been shown to be a problem with sampling volumes of 325 m^3).

3.3 The amount of air sampled through the adsorbent cartridge is recorded, and the cartridge is placed in an appropriately labeled container and shipped along with blank adsorbent cartridges to the analytical laboratory for analysis.

3.4 The filters and PUF adsorbent cartridge are extracted together with benzene. The extract is concentrated, diluted with hexane, and cleaned up using column chromatography.

3.5 The High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) system is verified to be operating properly and is calibrated with five concentration calibration solutions, each analyzed in triplicate.

3.6 A preliminary analysis of a sample of the extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

3.7 The samples and the blanks are analyzed by HRGC/HRMS and the results are used (along with the amount of air sampled) to calculate the concentrations of polychlorinated dioxins in ambient air.

4. Significance

4.1 Polychlorinated dibenzo-p-dioxins (PCDDs) are extremely toxic. They are carcinogenic and are of major environmental concern. Certain isomers, for example, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), have LD50 values in the parts-per-trillion range for some animal species. Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCBs). Recently, however, combustion sources have been shown to emit polychlorinated dibenzo-p-dioxin (PCDD), including the open-flame combustion of wood containing chlorophenol wood preservatives, and emissions from burning transformers and/or capacitors that contain PCBs and chlorobenzenes.

4.2 Several documents have been published which describe sampling and analytical approaches for PCDDs, as outlined in Section 2.2. The attractive features of these methods have been combined in this procedure. This method has not been validated in its final form, and, therefore, one must use caution when employing it for specific applications.

4.3 The relatively low level of PCDDs in the environment requires the use of high volume sampling techniques to acquire sufficient samples for analysis. However, the volatility of PCDDs prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most PCDDs.

5. Definitions

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356 and E355 (Sections 2.1.1 and 2.1.3). All abbreviations and symbols within this document are defined the first time they are used.

6. Interferences

6.1 Chemicals that elute from the gas chromatographic (GC) column within ±10 scans of the standards or compounds of interest and which produce, within the retention time windows, ions with any mass-to-charge (m/e) ratios close enough to those of the ion fragments used to detect or quantify the analyte compounds are potential interferences. Most frequently encountered potential interferences are other sample components that are extracted along with PCDDs, e.g., polychlorinated biphenyls (PCBs), methoxybiphenyls, chlorinated hydroxydiphenylethers, chlorinated naphthalenes, DDE, DDT, etc. The actual incidence of interference by these compounds also depends upon relative concentrations, mass spectrometric resolution, and chromatographic conditions. Because very low levels of PCDDs must be measured, the elimination of interferences is essential. High-purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory reagent blanks must be analyzed to demonstrate absence of contamination that would interfere with the measurements. Column chromatographic procedures are used to remove some coextracted sample components; these procedures must be performed carefully to minimize loss of analyte compounds during attempts to increase their concentration relative to other sample components.

6.2 In addition to chemical interferences, inaccurate measurements could occur if PCDDs are retained on particulate matter, the filter, or PUF adsorbent cartridge, or are chemically changed during sampling and storage in ways that are not accurately measured by adding isotopically labeled spikes to the samples.

6.3 The system cannot separately quantify gaseous PCDDs and particulate PCDDs because the material may be lost from the filter by volatilization after collection and may be transferred to the absorbent cartridge. Gaseous PCDDs may also be adsorbed on particulate matter on the filter.

7. Apparatus

7.1 General Metal Works (GMW) Model PS-1 Sampler.

7.2 At least two Model PS-1 sample cartridges and filters per PS-1 Sampler.

7.3 Calibrated GMW Model 40 calibrator.

7.4 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS)

7.4.1 The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 2-uL injection volume is used consistently. With some GC injection ports, however, 1-uL injections may produce some improvement in precision and chromatographic separation. A 1-uL injection volume may be used if adequate sensitivity and precision can be achieved.

[NOTE: If 1 uL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 uL.]

7.4.2 Gas Chromatograph-Mass Spectrometer Interface.
The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless

steel. The interface components should be compatible with 300°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb TCDD. Vespel® or equivalent ferrules are recommended.

7.4.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less (Section 12.3.4.1). At a minimum, ions that occur at the following masses must be monitored:

2,3,7,8-TCDD	1,2,3,4,7,8-H_xCDD	OCDD
258.9300	326.8521	394.7742
319.8965	389.8156	457.7377
321.8936	391.8127	459.7347
331.9368		
333.93338		

7.4.4 Data System. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.

7.4.5 GC Column. A fused silica column (30 m x 0.25 mm I.D.) coated with DB-5, 0.25 u film thickness (J & S Scientific, Inc., Crystal Lake, IL) is utilized to separate each of the several tetra- through octa-PCDDs, as a group, from all of the other groups. This column also resolves 2,3,7,8-TCDD from all 21 other TCDD isomers; therefore, 2,3,7,8-TCDD can be determined quantitatively if proper calibration procedures are followed as per Sections 12.3 through 12.6. Other columns may be used for determination of PCDDs, but separation of the wrong PCDD isomers must be demonstrated and documented. Minimum acceptance criteria must be determined as per Section 12.1. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

7.5 All required syringes, gases, and other pertinent supplies to operate the HRGC/HRMS system.

7.6 Airtight, labeled screw-capped containers to hold the sample cartridges (perferably glass with Teflon seals or other noncontaminating seals).

7.7 Data sheets for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

7.8 Balance capable of weighing accurately to $\pm$0.001 g.

7.9 Pipettes, micropipets, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 uL and 100 uL of isotopically labeled dioxin solutions.

7.10 Soxhlet extractors capable of extracting GMW PS-1 PUF adsorbent cartridges (2.3" x 5" length), 500-mL flask, and condenser.

7.11 Vacuum drying oven system capable of maintaining the PUF cartridges being evacuated at 240 torr (flushed with nitrogen) overnight.

7.12 Ice chest - to store samples at 0°C after collection.

7.13 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents reagents, etc.

7.14 Adsorbtion columns for column chromatography - 1 cm x 10 cm and 1 cm x 30 cm, with stands.

7.15 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.

7.16 Laboratory refrigerator with chambers operating at 0°C and 4°C.

7.17 Kuderna-Danish apparatus - 500 mL evaporating flask, 10 mL graduated concentrator tubes with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-570001-0500, K-50300-0121, and K-569001-219, or equivalent).

7.18 Two-ball micro Snyder Column, Kuderna-Danish (Kontes 569001-0219, or equivalent).

7.19 Stainless steel spatulas and spoons.

7.20 Minivials - 1 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon-faced silicone disks, and a vial holder.

7.21 Chromatographic columns for Carbopak cleanup - disposable 5-mL graduated glass pipets, 6 to 7 mm ID.

7.22 Desiccator.

7.23 Polyester gloves for handling PUF cartridges and filter.

7.24 Die - to cut PUF plugs.

7.25 Water bath equipped with concentric ring cover and capable of being temperature-controlled within $\pm$2°C.

7.26 Erlenmeyer flask, 50 mL.

7.27 Glass vial, 40 mL.

7.28 Cover glass petri dishes for shipping filters.

7.29 Fritted glass extraction thimbles.

7.30 Pyrex glass tube furnace system for activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

[NOTE: Reuse of glassware should be minimized to avoid the risk of cross-contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8. Reagents and Materials

8.1 Ultrapure glass wool, silanized, extracted with methylene chloride and hexane, and dried.

8.2 Ultrapure acid-washed quartz fiber filters for PS-1 Sampler (Pallfex 2500 glass, or equivalent).

8.3 Benzene (Burdick and Jackson, glass-distilled, or equivalent).

8.4 Hexane (Burdick and Jackson, glass-distilled, or equivalent).

8.5 Alumina, acidic - extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 190°C.

8.6 Silica gel - high-purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130°C.

8.7 Silica gel impregnated with 40 percent (by weight) sulfuric acid - prepared by adding two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated) and mixiing with a glass rod until free of lumps; stored in a screw-capped glass bottle.

8.8 Graphitized carbon black (Carbopak C or equivalent), surface of approximately 12 m^2/g, 80/100 mesh - prepared by thoroughly mixing 3.6 grams Carbopak C and 16.4 grams Celite 545® in a 40-mL vial and activating at 130°C for six hours; stored in a desiccator.

8.9 Sulfuric Acid, ultrapure, ACS grade, specific gravity 1.84.

8.10 Sodium Hydroxide, ultrapure, ACS grade.

8.11 Native and isotopically labeled PCDD/PCDF isomers for calibration and spiking standards, from Cambridge Isotopes, Cambridge, MA.

8.12 n-decane (Aldrich Gold Label grade [D90-1], or equivalent).

8.13 Toluene (high purity, glass-distilled).

8.14 Acetone (high purity, glass-distilled).

8.15 Filters, quartz fiber - Pallflex 2500 QAST, or equivalent.

8.16 Ultrapure nitrogen gas (Scott chromatographic grade, or equivalent).

8.17 Methanol (chromatographic grade).

8.18 Methylene chloride (chromatographic grade, glass-distilled).

8.19 Dichloromethane/hexane (3:97, v/v), chromatographic grade.

8.20 Hexane/dichloromethane (1:1, v/v), chromatogtraphic grade.

8.21 Perfluorokerosene (PFK), chromatographic grade.

8.22 Celite 545®, reagent grade, or equivalent.

8.23 Membrane filters or filter paper with pore sizes less than 25 um, hexane-rinsed.

8.24 Granular anhydrous sodium sulfate, reagent grade.

8.25 Potassium carbonate-anhydrous, granular, reagent grade.

8.26 Cyclohexane, glass-distilled.

8.27 Tridecane, glass-distilled.

8.28 2,2,3-trimethylpentane, glass-distilled.

8.29 Isooctane, glass-distilled.

8.30 Sodium sulfate, ultrapure, ACS grade.

8.31 Polyurethane foam - 3 inches thick sheet stock, polyether type used in furniture upholstering, density 0.022 g/cm^3.

8.32 Concentration calibration solutions (Table 1) - four tridecane solutions containing $^{13}C_{12}$-1,2,3,4-TCDD (recovery standard) and unlabeled 2,3,7,8-TCDD at varying concentrations, and $^{13}C_{12}$-2,3,7,8-TCDD (internal standard, CAS RN 80494-19-5). These solutions must be obtained from the Quality Assurance Division, U.S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada, and must be used to calibrate the instrument. However, secondary standards may be obtained from commercial sources, and solutions may be prepared in the analytical laboratory. Traceability of standards must be verified against EPA-supplied standard solutions by procedures documented in laboratory SOPs. Care must be taken to use the correct standard. Serious overloading of instruments may occur if concentration calibration solutions intended for low-resolution MS are injected into the high-resolution MS.

8.33 Column performance check mixture dissolved in 1 mL of tridecane from Quality Assurance Division (EMSL-LV). Each ampule of this solution will contain approximately 10 ng of the following components (A) eluting near 2,3,7,8-TCDD and of the first (F) and last-eluting (L) TCDDs, when using the recommended columns at a concentration of 10 pg/uL of each of these isomers:

- o unlabeled 2,3,7,8-TCDD
- o $^{13}C_{12}$-2,3,7,8-TCDD
- o 1,2,3,4-TCDD (A)
- o 1,4,7,8-TCDD (A)
- o 1,2,3,7-TCDD (A)
- o 1,2,3,8-TCDD (A)
- o 1,3,6,8-TCDD (F)
- o 1,2,8,9-TCDD (L)

If these solutions are unavailable from EPA, they should be prepared by the analytical laboratory or a chemical supplier and analyzed in a manner traceable to the EPA performance check mixture designed for 2,3,7,8-TCDD monitoring. Similar mixtures of isotopically labeled compounds should be prepared to check performance for monitoring other specific forms of TCDD that are of interest.

8.34 Sample fortification solution - isooctane solution containing the internal standard at a nominal concentration of 10 pg/uL.

8.35 Recovery standard spiking solution - tridecane solution containing the isotopically labeled standard ($^{13}C_{12}$-2,3,7,8-TCDD and other PCDDs of interest) at a concentration of 10.0 pg/uL.

8.36 Field blank fortification solutions - isooctane solutions containing the following:

- Solution A: 10.0 pg/uL of unlabeled 2,3,7,8-TCDD
- Solution B: 10.0 pg/uL of unlabeled 1,2,3,4-TCDD

[NOTE: These reagents and the detailed analytical procedures described herein are designed for monitoring TCDD isomer concentrations of 6.0 pg/m^3 to 37 pg/m^3 each. If ambient concentrations should exceed these levels, concentrations of calibrations and spiking solutions will need to be modified, along with the detailed sample preparation procedures. The reagents and procedures described herein are based on Appendix B of the Protocol for the Analysis of 2,3,7,8-TCDD (Section 2.2.2) combined with the evaluation of the high volume air sampler for PCDD.

9. Preparation of PUF Sampling Cartridge

9.1 The PUF adsorbent is a polyether-type polyurethane foam (density No. 3014 or 0.0225 g/cm^3) used for furniture upholstery.

9.2 The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.

9.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

9.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

9.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.

9.6 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 11, before the batch is considered acceptable for field use. A blank level of <10 ng/plug for single compounds is considered to be acceptable.

10. Sample Collection

10.1 Description of Sampling Apparatus

10.1.1 The entire sampling system is diagrammed in Figure 2. A unit specifically designed for this method is commercially available (Model PS-1 - General Metal Works, Inc., Village of Cleves, Ohio).

10.1.2 The sampling module (Figure 1) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF is retained in the glass sampling cartridge.

10.2 Calibration of Sampling System

10.2.1 The airflow through the sampling system is monitored by a Venturi/Magnehelic assembly, as shown in Figure 2. Assembly must be audited every six months using an audit calibration orifice, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single-point calibration must be performed before and after each sample collection, using the procedure described in Section 10.2.2.

10.2.2 Prior to calibration, a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate is indicated on the Magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warm up for 10 minutes and then the flow control

valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should be recorded on an appropriate data sheet.

10.2.3 The calibration orifice is placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded after a stable reading is achieved. The sampler is then shut off.

10.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in Section 10.2.3, and the calibration curve for the Venturi/ Magnehelic assembly is used to calculate sample flow from the data obtained in Section 10.2.2. The calibration data should be recorded on an appropriate data sheet. If the two values do not agree within 10%, the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found, the sampler should be recalibrated (multipoint) according to the U.S. EPA High Volume Sampling Method (Section 10.2.1).

10.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

10.3 Sample Collection

10.3.1 After the sampling system has been assembled and calibrated as described in Sections 10.1 and 10.2, it can be used to collect air samples, as described in Section 10.3.2.

10.3.2. The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air.

10.3.3 A clean PUF sampling cartridge and quartz filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into the sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.

10.3.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number are recorded on a suitable data sheet, as illustrated in Figure 3.

10.3.5 The voltage variator and flow control valve are placed at the settings used in Section 10.2.3, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.

10.3.6 The Magnehelic reading is recorded every six hours during the sampling period. The calibration curve (Section 10.2.4) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.

10.3.7 At the end of the desired sampling period, the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.

10.3.8 The Magnehelic calibration is checked using the calibration orifice, as described in Section 10.2.4. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.

10.3.9 At least one field filter/PUF blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/PUF cartridge assembly.

10.3.10 Samples are stored at 20°C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4°C.

11. Sample Extraction

11.1 Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of benzene and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the benzene to a clean glass container, and obtain it as a blank for later analysis, if required. After cooling, spike the cartridges and filters with an internal standard (Table 1). After spiking, place the PUF cartridge and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional). (The filter and PUF cartridge are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.) Add 200 to 250 mL of benzene to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.

11.2 Transfer the extract to a Kuderna-Danish (K-D) apparatus, concentrate it to 2 to 3 mL, and let it cool. Rinse the column and flask with 5 mL of benzene, collecting the rinsate in the concentrator tube to 2 to 3 mL. Repeat the rinsing and concentration steps twice more. Remove the concentrator tube from the K-D apparatus and carefully reduce the extract volume to approximately 1 mL with a stream of nitrogen using a flow rate and distance above the solution such that a gentle rippling of the solution surface is observed.

11.3 Perform the following column chromatographic procedures for sample extraction cleanup. These procedures have been demonstrated to be effective for a mixture consisting of:

- 1,2,3,4-TCDD
- 1,2,3,4,7,8-H_xCDD
- OCDD
- 2,3,7,8-TCDD

11.3.1 Prepare an acidic silica gel column as follows (Figure 4): Pack a 1 cm x 10 cm chromatographic column with a glass wool plug, a 1-cm layer of Na_2SO_4/K_2CO_3 (1:1), 1.0 g of silica gel (Section 8.6), and 4.0 g of 40-percent (w/w) sulfuric acid-impregnated silica gel (Section 8.7). Pack a second chromatographic column (1 cm x 30 cm) with a glass wool plug and 6.0 g of acidic alumina (Section 8.5), and top it with a 1-cm layer of sodium sulfate (Section 8.30). Add hexane to the columns until they are free of channels and air bubbles.

11.3.2 Quantitatively transfer the benzene extract (1 mL) from the concentrator tub to the top of the silica gel column. Rinse the concentrator tube with 0.5-mL portions of hexane. Transfer the rinses to the top of the silica gel column.

11.3.3 Elute the extract from the silica gel column with 90 of mL hexane directly into a Kudena-Danish concentrator tube. Concentrate the eluate to 0.5 mL, using nitrogen blowdown, as necessary.

11.3.4 Transfer the concentrate (0.5 mL) to the top of the alumina column. Rinse the K-D assembly with two 0.5-mL portions of hexane, and transfer the rinses to the top of the alumina column. Elute the alumina column with 18 mL hexane until the hexane level is just below the top of the sodium sulfate. Discard the eluate. Do not let the columns reach dryness (i.e., maintain a solvent "head").

11.3.5 Place 30 mL of 20% (v/v) methylene chloride in hexane on top of the alumina column and elute the TCDDs from the column. Collect this fraction in a 50-mL Erlenmeyer flask.

11.3.6 Certain extracts, even after cleanup by column chromatography, contain interferences that preclude determination of TCDD at low parts-per-trillion levels. Therefore, a cleanup step is included using activated carbon which selectively retains planar molecules such as TCDDs. The TCDDs are then removed from the carbon by elution with toluene. Proceed as follows: Prepare an 18% Carbopak C/Celite 545® mixture by thoroughly mixing 3.6 grams Carbopak C (80/100 mesh) and 16.4 grams Celite 545® in a 40-mL vial. Activate the mixture at 130°C for 6 hours, and store it in a desiccator. Cut off a clean 5-mL disposable glass pipet at the 4-mL mark. Insert a plug of glass wool (Section 8.1) and push it to the 2-mL mark. Add 340 mg of the activated Carbopak/Celite mixture followed by another glass wool plug. Using two glass rods, push both glass wool plugs simultaneously toward the Carbopak/Celite plug to a length of 2.0 to 2.5 cm. Pre-elute the column with 2 mL of toluene followed by 1 mL of 75:20:5 methylene chloride/methanol/ benzene, 1 mL of 1:1 cyclohexane in methylene choride, and 2 mL of hexane. The flow rate should be less than 0.5 mL per minute. While the column is still wet with hexane, add the entire elute (30 mL) from the alumina column (Section 11.3.5) to the top of the column. Rinse the Erlenmeyer flask that contained the extract twice with 1 mL of hexane and add the rinsates to the top of the column. Elute the column sequentially with two 1-mL aliquots of hexane, 1 mL of 1:1 cyclohexane in methylene chloride, and 1 mL of 75:20:5 methylene

chloride/mentanol/benzene. Turn the column upside down and elute the TCDD fraction into a concentrator tube with 6 mL of toluene. Warm the tube to approximately 60°C and reduce the toluene volume to approximately 1 mL using a stream of nitrogen. Carefully transfer the residue into a 1-mL minivial and, again at elevated temperature, reduce the volume to about 100 uL using a stream of nitrogen. Rinse the concentrator tube with 3 washings using 200 uL of 1% toluene in CH_2Cl_2 each time. Add 50 uL of tridecane and store the sample in a refrigerator until GC/MS analysis is performed.

12. HRGC/HRMS System Performance Criteria

The laboratory must document that the system performance criteria specified in Sections 12.1, 12.2, and 12.3 have been met before analysis of samples.

12.1 GC Column Performance

12.1.1 Inject 2 uL of the column performance check solution (Section 8.3) and acquire selected ion monitoring (SIM) data for m/z 258.930, 319.897, 321.894, and 333.933 within a total cycle time of $\leq$1 second.

12.1.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of $\leq$25%, where

$$\text{Valley Percent} = (x/y)(100)$$

x = measured distance from extroplated baseline to minimum of valley; and

y = the peak height of 2,3,7,8-TCDD.

[Note: It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this protocol, thus defining

the retention time window for total TCDD determination. The peaks representing 2,3,7,8-TCDD, and the first and last eluting TCDD isomers must be labeled and identified.]

12.2 Mass Spectometer Performance

12.2.1 The mass spectrometer must be operated in the electron (impact) ionization mode. Static mass resolution of at least 10,000 (10% valley) must be demonstrated before any analysis of a set of samples is performed (Section 12.2.2). Static resolution checks must be performed at the beginning and at the end of each 12-hour period of operation. However, it is recommended that a visual check (e.g., not documented) of the static resolution be made using the peak matching unit before and after each analysis.

12.2.2 Chromatography time for TCDD may exceed the long-term mass stability of the mass spectrometer; therefore, mass drift correction is mandatory. A reference compound (high boiling perfluorokerosene [PFK] is recommended) is introduced into the mass spectrometer. An acceptable lock mass ion at any mass between m/z 250 and m/z 334 (m/z 318.979 from PFK is recommended) must be used to monitor and correct mass drifts.

[NOTE: Excessive PFK may cause background noise problems and contamination of the source, resulting in an increase in "downtime" for source cleaning. Using a PFK molecular leak, tune the instrument to meet the minimum required mass resolution of 10,000 (10% valley) at m/z 254.986 (or any other mass reasonably close to m/z 259). Calibrate the voltage sweep at least across the mass range m/z 259 to m/z 344 and verify that m/z 330.979 from PFK (or any other mass close to m/z 334) is measured within $\pm$5 ppm (i.e., 1.7 mmu). Document the mass resolution by recording the peak profile of the PFK reference peak m/z 318.979 (or any other reference peak at a mass close to m/z 320/322). The format of the peak profile representation must allow manual determination of the resolution;

i.e., the horizontal axis must be a calibrated mass scale (mmu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum) must appear on the hard copy and cannot exceed 31.9 mmu or 100 ppm.]

12.3 Initial Calibration

Intitial calibration is required before any samples are analyzed for 2,3,7,8-TCDD. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 12.6.

12.3.1 All concentration calibration solutions listed in Table 1 must be utilized for the initial calibration.

12.3.2 Tune the instrument with PFK as described in Section 12.2.2.

12.3.3 Inject 2 uL of the column performance check solution (Section 8.33) and acquire SIM mass spectral data for m/z 258.930, 319.897, 321.894, 331.937, and 333.934 within a total cycle time of $\leq$1 second. The laboratory must not perform any further analysis until it has been demonstrated and documented that the criterion listed in Section 12.1.2 has been met.

12.3.4 Using the same GC (Section 12.1) and MS (Section 12.2) conditions that produced acceptable results with the column performance check solution, analyze a 2-uL aliquot of each of the 5 concentration calibration solutions in triplicate with the gas chromatographic operating parameters shown in Table 2.

12.3.4.1 Total cycle time for data acquisition must be $\leq$1 second. Total cycle time includes the sum of all the dwell times and voltage reset times.

12.3.4.2 Acquire SIM data for the following selected characteristic ions:

m/z	Compound
258.930	TCDD - COCl
319.897	unlabeled TCDD
321.894	unlabeled TCDD
331.937	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD
333.934	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD

12.3.4.3 The ratio of intergrated ion current for m/z 319.897 to m/z 321.894 for 2,3,7,8-TCDD must be between 0.67 and 0.87 ($\pm$13%).

12.3.4.4 The ratio of integrated ion current for m/z 331.937 to m/z 333.934 for $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD must be between 0.67 and 0.87.

12.3.4.5 Calculate the relative response factor for unlabeled 2,3,7,8-TCDD [RRF(I)] relative to $^{13}C_{12}$-2,3,7,8-TCDD and for labeled $^{13}C_{12}$-2,3,7,8-TCDD [RRF(II)] relative to $^{13}C_{12}$-1,2,3,4-TCDD as follows:

$$RRF(I) = \frac{A_x \cdot Q_{IS}}{Q_x \cdot A_{IS}}$$

$$RRF(II) = \frac{A_{IS} \cdot Q_{RS}}{Q_{IS} \cdot A_{RS}}$$

where:

A_x = sum of the integrated abundances of m/z 319.897 and m/z 321.894 for unlabeled 2,3,7,8,-TCDD.

A_{IS} = sum of the integrated abundances of m/z 331.937 and m/z 333.934 for $^{13}C_{12}$-2,3,7,8-TCDD.

A_{RS} = sum of the integrated abundances for m/z 331.937 and m/z 333.934 for $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{IS} = quantity (pg) of $^{13}C_{12}$-2,3,7,8-TCDD injected.

Q_{RS} = quantity (pg) of $^{13}C_{12}$-1,2,3,4-TCDD injected.

Q_x = quantity (pg) of unlabeled 2,3,7,8-TCDD injected.

12.4 Criteria for Acceptable Calibration

The criteria listed below for acceptable calibration must be met before analysis of any sample is performed.

12.4.1 The percent relative standard deviation (RSD) for the response factors from each of the triplicate analyses for both unlabeled and $^{13}C_{12}$-2,3,7,8-TCDD must be less than $\pm$20%.

12.4.2 The variation of the five mean RRFs for unlabeled 2,3,7,8-TCDD obtained from the triplicate analyses must be less than $\pm$20% RSD.

12.4.4 SIM traces for $^{13}C_{12}$-2,3,7,8-TCDD must present a signal-to-noise ratio $\geq$10 for 333.934.

12.4.5 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

[NOTE: If the criteria for acceptable calibration listed in Sections 12.4.1 and 12.4.2 have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The mean RRF from five triplicate determinations for unlabeled 2,3,7,8-TCDD and for $^{13}C_{12}$2,3,7,8-TCDD will be used for all calculations until routine calibration criteria (Section 12.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of five triplicate determinations.]

12.5 Routine Calibration

Routine calibration must be performed at the beginning of each 12-hour period after successful mass resolution and GC column performance check runs.

12.5.1 Inject 2 uL of the concentration calibration solution (Section 8.32) that contains 5.0 pg/uL of unlabeled 2,3,7,8-TCDD, 10.0 pg/uL of $^{13}C_{12}$-2,3,7,8-TCDD, and 5.0 pg/uL $^{13}C_{12}$-1,2,3,4-TCDD. Using the same GC/MS/DS conditions as in Sections 12.1, 12.2, and 12.3, determine and document acceptable calibration as provided in Section 12.6.

12.6 Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken and the instrument must be recalibrated.

12.6.1 The measured RRF for unlabeled 2,3,7,8-TCDD must be within $\pm$20 percent of the mean values established (Section 12.3.4.5) by triplicate analyses of concentration calibration solutions.

12.6.2 The measured RRF for $^{13}C_{12}$-2,3,7,8-TCDD must be within $\pm$20 percent of the mean value established by triplicate analyses of concentration calibration solutions (Section 12.3.4.5).

12.6.3 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

12.6.4 If one of the above criteria is not satisfied, a second attempt can be made before repeating the entire initialization process (Section 12.3).

[NOTE: An initial calibration must be carried out whenever any HRCC solution is replaced.]

13. Analytical Procedures

13.1 Remove the sample extract or blank from storage, allow it to warm to ambient laboratory temperature, and add 5 uL of recovery standard solution. With a stream of dry, purified nitrogen, reduce the extract/blank volume to 20 uL.

13.2 Inject a 2-uL aliquot of the extract into the GC, which should be operating under the conditions previously used (Section 12.1) to produce acceptable results with the performance check solution.

13.3 Acquire SIM data using the same acquisition time and MS operating conditions previously used (Section 12.3.4) to determine the relative response factors for the following selected characteristic ions:

m/z	Compound
258.930	TCDD - COCl (weak at detection limit level)
319.897	unlabeled TCDD
321.894	unlabeled TCDD
331.937	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD,
333.934	$^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD,

13.4 Identification Criteria

13.4.1 The retention time (RT) (at maximum peak height) of the sample component m/z 319.897 must be within -1 to +3 seconds of the retention time of the peak for the isotopically labeled internal standard at m/z 331.937 to attain a positive identification of 2,3,7,8-TCDD. Retention times of other tentatively identified TCDDs must fall within the RT window established by analyzing the column performance check solution (Section 12.1). Retention times are required for all chromatograms.

13.4.2 The ion current responses for m/z 258.930, 319.897 and 321.894 must reach their maxima simultaneously ($\pm$1 scan), and all ion current intensities must be $\geq$2.5 times noise level for positive identification of a TCDD.

13.4.3 The integrated ion current at m/z 319.897 must be between 67 and 87 percent of the ion current response at m/z 321.894.

13.4.4 The integrated ion current at m/z 331.937 must be between 67 and 87 percent of the ion current response at m/z 333.934.

13.4.5 The integrated ion currents for m/z 331.937 and 333.934 must reach their maxima within ±1 scan.

13.4.6 The recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD must be between 40 and 120 percent.

14. Calculations

14.1 Calculate the concentration of 2,3,7,8-TCDD (or any other TCDD isomer) using the formula:

$$C_X = \frac{A_X \cdot Q_{IS}}{A_{IS} \cdot V \cdot \overline{\overline{RRF}}(I)}$$

where:

C_X = quantity (pg) of unlabeled 2,3,7,8-TCDD (or any other unlabeled TCDD isomer) present.

A_X = sum of the integrated ion abundances determined for m/z 319.897 and 321.894.

A_{IS} = sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}C_{12}$-2,3,7,8-TCDD (IS = internal standard).

Q_{IS} = quantity (pg) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction (Q_{IS} = 500 pg).

V = volume (m^3) of air sampled.

$\overline{\overline{RRF}}(I)$ = Calculated mean relative response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD. This value represents the grand mean of the RRF(I)s obtained in Section 12.3.4.5.

14.2 Calculate the recovery of the internal standard $^{13}C_{12}$-2,3,7,8-TCDD, measured in the sample extract, using the formula:

$$\text{Internal standard, percent recovery} = \frac{A_{IS} \cdot Q_{RS}}{A_{RS} \cdot \overline{RRF(II)} \cdot Q_{IS}} \times 100$$

where:

A_{IS} and Q_{IS} = same definitions as above (Section 14.1)

A_{RS} = sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of $^{13}C_{12}$-1,2,3,4-TCDD (RS = recovery standard).

Q_{RS} = quantity (pg) of $^{13}C_{12}$-1,2,3,4-TCDD added to the sample residue before HRGC-HRMS analysis (Q_{RS} = 500 pg).

RRF(II) = Calculated mean relative response factor for labeled $^{13}C_{12}$-2,3,7,8-TCDD. This value represents the grand mean of the RRF(II)s calculated in Section 12.3.4.5.

14.3 Total TCDD Concentration

14.3.1 All positively identified isomers of TCDD must be within the RT window and meet all identification criteria listed in Sections 13.4.2, 13.4.3, and 13.4.4. Use the expression in Section 14.1 to calculate the concentrations of the other TCDD isomers, with C_X becoming the concentration of any unlabeled TCDD isomer.

14.4 Estimated Detection Limit

14.4.1 For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the <u>estimated</u> minimum detectable concentration. The background area is determined by integrating the ion abundances for m/z 319.897 and 321.894 in the appropriate region and relating that height area to an estimated concentration that would produce that product area. Use the formula:

$$CE = \frac{(2.5) \cdot (A_x) \cdot (Q_{IS})}{(A_{IS}) \cdot \overline{RRF(I)} \cdot (W)}$$

where:

C_E = estimated concentration of unlabeled 2,3,7,8-TCDD required to produce A_x.

A_x = sum of integrated ion abundance for m/z 319.897 and 321.894 in the same group of $\geq$25 scans used to measure A_{IS}.

A_{IS} = sum of integrated ion abundance for the appropriate ion characteristic of the internal standard, m/z 331.937 and m/z 333.934.

Q_{IS}, $\overline{RRF(I)}$, and V retain the definitions previously stated in Section 14.1. Alternatively, if peak height measurements are used for quantification, measure the estimated detection limit by the peak height of the noise in the TCDD RT window.

14.5 The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S_1 - S_2|}{(\text{Mean Concentration})} = \frac{|S_1 - S_2|}{(S_1 + S_2)/2} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

14.6 The total sample volume (V_m) is calculated from the periodic flow readings (Magnehelic) taken in Section 10.3.6 using the following equation:

$$V_m = \frac{Q_1 + Q_2 \cdots Q_N}{N} \times \frac{T}{1000}$$

where:

V_m = total sample volume (m^3).

$Q_1\ Q_2 \cdots Q_N$ = flow rates determined at the beginning, end, and intermediate points during sampling (L/minute).

N = number of data points averaged.

T = elapsed sampling time (minutes).

14.7 The concentration of compound in the sample is calculated using the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where:

V_s = total sample volume (m^3) at 25°C and 760 mm Hg pressure.
V_m = total sample flow (m^3) under ambient conditions.
P_A = ambient pressure (mm Hg).
t_A = ambient temperature (°C).

14.8 The concentration of compound in the sample is calculated using the following equation:

$$C_A = \frac{A \times V_E}{V_i \times V_s}$$

where:

C_A = concentration (ug/m^3) of analyte in the sample.
A = calculated amount of material determined by HRGC/HRMS.
V_i = volume (uL) of extract injected.
V_E = final volume (mL) of extract.
V_s = total volume (m^3) of air samples corrected to standard conditions.

15. Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities in their laboratory: 1) assembly, calibration and operation of the sampling system with make and model of equipment used; 2) preparation, purification, storage, and handling of sampling cartridges and filters; 3) assembly, calibration and operation of the HRGC/HRMS system with make and model of equipment used; 4) all aspects of data recording and processing, including lists of computer hardware and software used.

15.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

15.2 Process, Field, and Solvent Blanks

15.2.1 One PUF cartridge and filter from each batch of approximately 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as process blank.

15.2.2 During each sampling episode, at least one PUF cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

15.2.3 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge or filter included) should be carried through the procedure and analyzed.

TABLE 1
COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

Recovery Standards		Analyte	Internal Standard
	$^{13}C_{12}$-1,2,3,4-TCDD	2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
HRCC1	2.5 pg/uL	2.5 pg/uL	10.0 pg/uL
HRCC2	5.0 pg/uL	5.0 pg/uL	10.0 pg/uL
HRCC3	10.0 pg/uL	10.0 pg/uL	10.0 pg/uL
HRCC4	20.0 pg/uL	20.0 pg/uL	10.0 pg/uL
HRCC5	40.0 pg/uL	40.0 pg/uL	10.0 pg/uL

Sample Fortification Solution

5.0 pg/uL of $^{13}C_{12}$-2,3,7,8-TCDD

Recovery Standard Spiking Solution

100 pg/uL $^{13}C_{12}$-1,2,3,4-TCDD

Field Blank Fortification Solutions

A) 4.0 pg/uL of unlabeled 2,3,7,8-TCDD

B) 5.0 pg/uL of unlabeled 1,2,3,4-TCDD

TABLE 2

RECOMMENDED GC OPERATING CONDITIONS

Column coating	SP-2330 (SP 2331)	CP-SIL 88
Film thickness	0.20 um	0.22 um
Column dimensions	60 m x 0.24 mm	50 m x 0.22 mm
Helium linear velocity	28-29 cm/sec at 240°C	28-29 cm/sec at 240°C
Initial temperature	200°C	190°C
Initial time	4 min	3 min
Temperature program	200°C to 250°C at 4°C/min	190°C to 240°C at 5°C/min

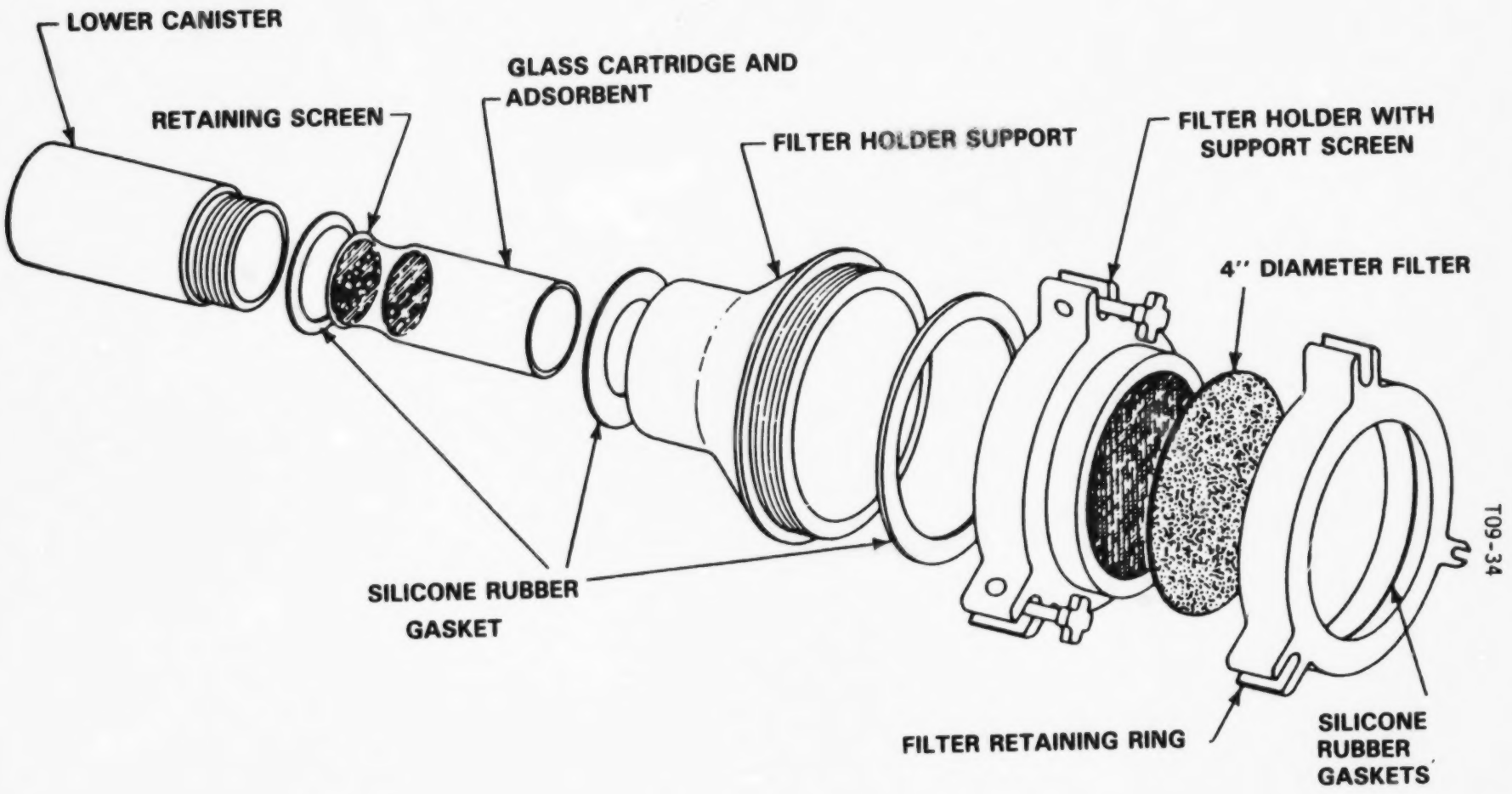


FIGURE 1. SAMPLING HEAD

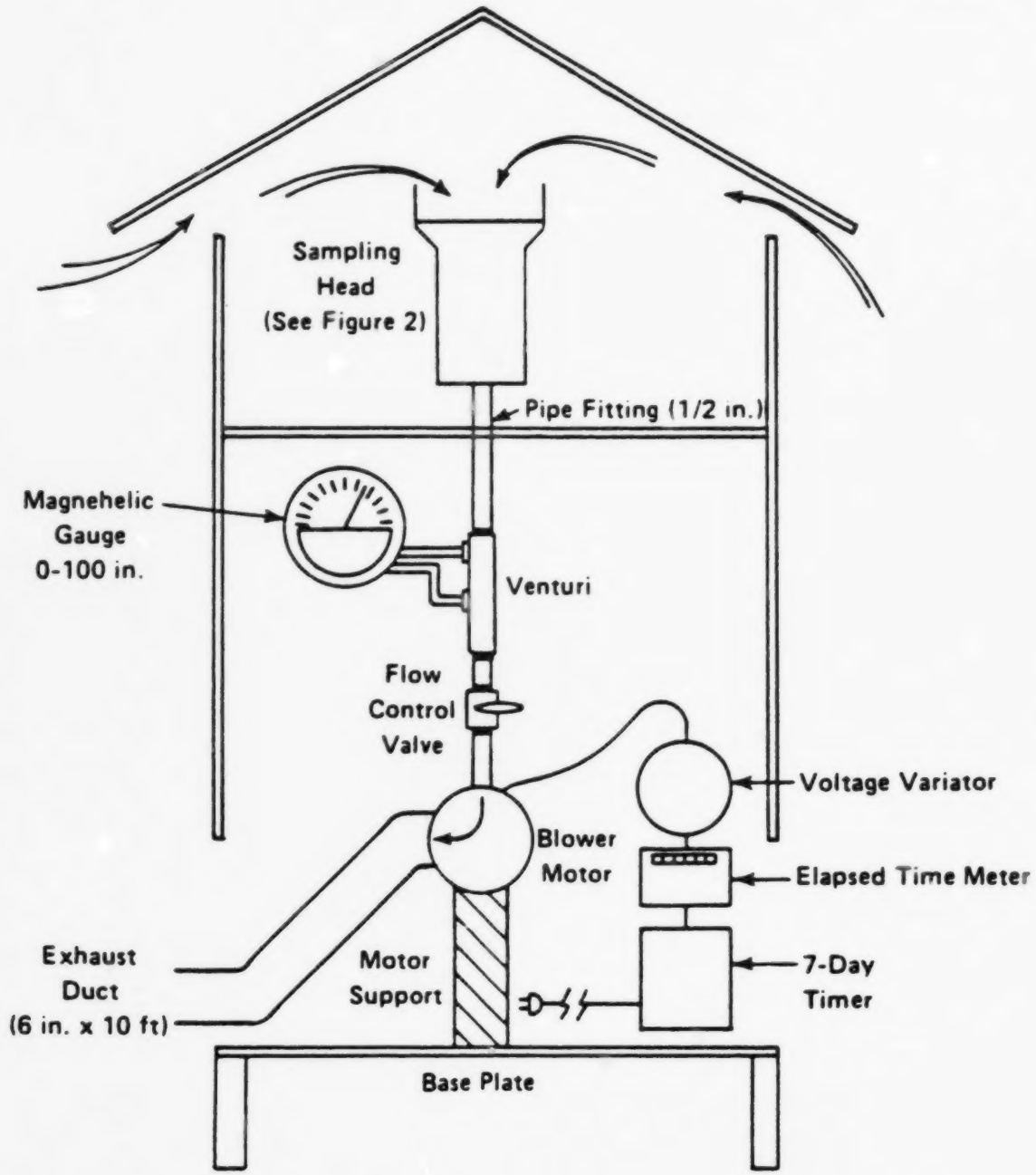


FIGURE 2. HIGH VOLUME AIR SAMPLER
GENERAL METAL WORKS (MODEL PS-1)

Performed by_____ Calibration Orifice S/N_____ Ambient Temperature_____°C

Date/Time_____ Manometer S/N _____ Bar. Press._____mm Hg

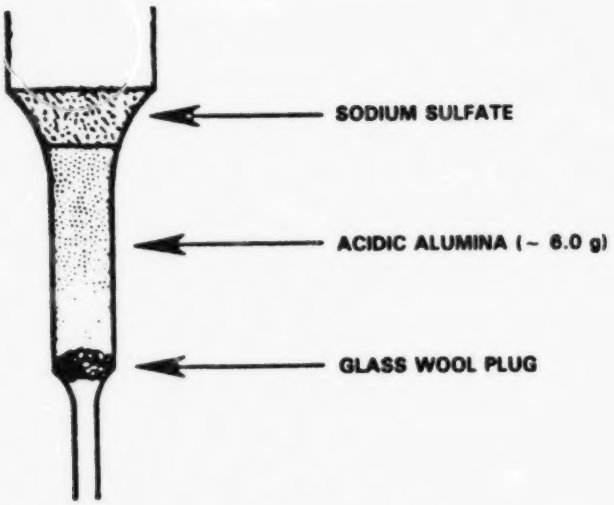
Sampler S/N	Variac Setting V	Timer OK? Yes/No	Calibration Orifice Data		Sampler Venturi Data		% Difference Between Calibration and Sample Venturi Flow Rates	Comments
			Manometer, in. H_2O	Flow Rate scm/min[a]	Magnehelic, in. H_2O	Flow Rate scm/min[b]		

(a) From Calibration Tables for Calibration Orifice or Venturi Tube
(b) From Calibration Tables for Venturi Tube in each Hi-Vol unit.

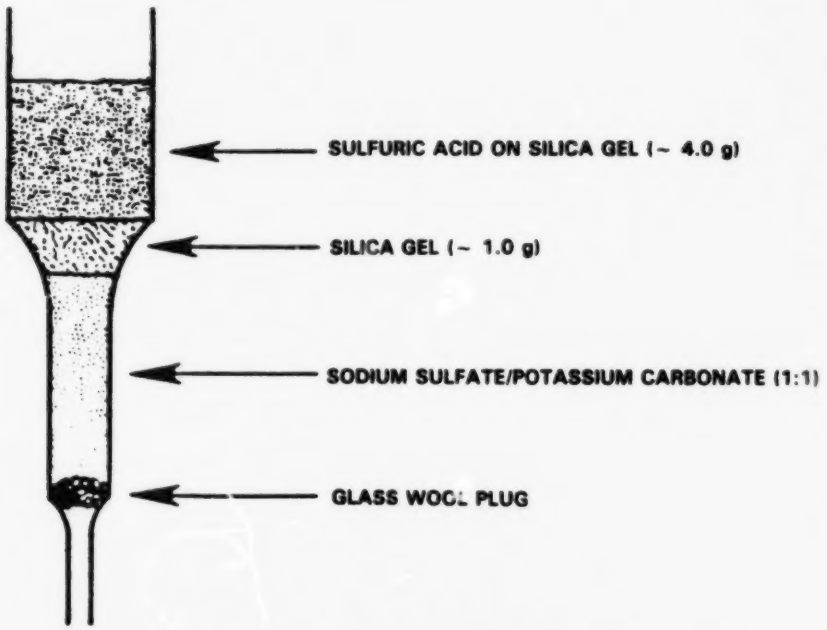
Date check by_____ Date _____

T09-36

FIGURE 3. EXAMPLE SAMPLING DATA SHEET



(a) ALUMINA COLUMN



(b) SILICA GEL COLUMN

FIGURE 4. MULTILAYERED EXTRACT CLEANUP COLUMNS

☆ U.S. GOVERNMENT PRINTING OFFICE : 1987-748-121/40692